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REVIEWS OF THE ENVIRONMENTAL EFFECTS OF POLLUTANTS:
III. CHROMIUM

UNITED STATES · ENVIRONMENTAL PROTECTION AGENCY

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REVIEWS OF THE ENVIRONMENTAL EFFECTS OF POLLUTANTS: III. CHROMIUM

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FOREWORD

A vast amount of published material is accumulating as numerous research investigations are conducted to develop a data base on the adverse effects of environmental pollution. As this information is amassed, it becomes continually more critical to focus on pertinent, well-designed studies. Research data must be summarized and interpreted in order to adequately evaluate the potential hazards of these substances to ecosystems and ultimately to public health. The Reviews of the Environmental Effects of Pollutants (REEPs) series represents an extensive compilation of relevant research and forms an up-to-date compendium of the environmental effect data on selected pollutants.

Reviews of the Environmental Effects of Pollutants: III. Chromium includes information on chemical and physical properties; pertinent analytical techniques; transport processes to the environment and subsequent distribution and deposition; impact on microorganisms, plants, and wildlife; toxicologic data in experimental animals including metabolism, toxicity, mutagenicity, teratogenicity, and carcinogenicity; and an assessment of its health effects in man. The large volume of factual information presented in this document is summarized and interpreted in the final chapter, "Environmental Assessment," which presents an overall evaluation of the potential hazard resulting from present concentrations of chromium in the environment. This final chapter represents a major contribution by James O. Pierce from the University of Missouri.

The REEPs are intended to serve various technical and administrative personnel within the Agency in the decision-making processes, i.e., in the development of criteria documents and environmental standards, and for other regulatory actions. The breadth of these documents makes them a useful resource for public health personnel, environmental specialists, and control officers. Upon request these documents will be made available to any interested individuals or firms, both in and out of the government. Depending on the supply, the document can be obtained directly by writing to:

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ABSTRACT

This study is a comprehensive, multidisciplinary review of the health and environmental effects of chromium and specific chromium compounds. Approximately 500 references are cited.

Chromium is abundant in the earth's crust and is widely dispersed in the environment. It is used extensively in refractory materials and chemicals, as a plating to produce hard and smooth surfaces, to prevent corrosion, and in manufacturing stainless and alloy steels. Major atmospheric emissions of chromium arise from metal producing industries, coal-fired plants, municipal incinerators, and cooling towers. Major releases to water are chiefly from the electroplating metal-finishing, textile, and tanning industries.

Harmful effects to man or animals seldom result from chromium in ambient air or public drinking water. Reported chromium toxicity occurs mainly from occupational exposure. Trivalent compounds are not highly toxic, but excessive exposure to dusts or mists of hexavalent chromium compounds produces dermatitis, skin lesions, and ulceration and perforation of the nasal septum, as well as liver and kidney damage. With long-term exposure to hexavalent chromium compounds, incidence of human lung cancer increases. No data suggest that these compounds are mutagenic or teratogenic risks.

Trace levels of chromium are essential to mammalian life. Irreversible metabolic damage may result from long-standing chromium deficiency. As a result of the refinement of many foods, diets in the United States are often low in chromium; organs of Americans usually contain less chromium than corresponding organs of people from other nations. Except in the lungs, tissue chromium content decreases progressively with age, which suggests that intake of biologically active chromium in the United States is marginal.

This report was submitted in partial fulfillment of Interagency Agreement No. D5-0403 between the Department of Energy and the U.S. Environmental Protection Agency. The draft report was submitted for review June 1976. The final report was completed in August 1977.

SECTION 1

SUMMARY

1.1 DISCUSSION OF FINDINGS

1.1.1 Chemical Properties and Analytical Techniques

Chromium, a transition element, is a steel gray, lustrous, hard metal which melts at 1857°C and boils at 2672°C and has valence states ranging from -2 to +6 (Section 2.2). A variety of chromium compounds are prepared from chromite ore. Most of these compounds contain chromium in the more stable trivalent and hexavalent oxidation states. The chromium in essentially all environmentally important chromium compounds is in one of these two oxidation states. Although tetravalent and pentavalent chromium compounds exist, they are unstable and decompose to hexavalent and trivalent chromium in aqueous solution (Section 2.2.4). The major chromium compounds produced are chromic oxide, chromic sulfide, chromic halides, and chromic sulfate. In aqueous solution, trivalent chromium forms a large array of hexacoordinate complexes with amines, water, urea, halides, sulfates, and organic acids (Section 2.2.3.5). Coordination complexes also occur with a variety of anions (Section 2.2.3.5). Olation occurs at alkaline pH; a wide range of polynuclear complexes are formed and ultimately precipitate as the olated complex $Cr(OH)_3 \cdot XH_2O$. All stable hexavalent chromium compounds are oxy compounds and are strong oxidants. Chromates (CrO_4^{2-}) and dichromates ($Cr_2O_7^{2-}$) are used to prepare other chromium compounds (Section 2.2.5).

The biochemistry of chromium is not completely known (Section 2.2.6). Chromium can react with nucleic acids and proteins. In reactions with proteins, it binds to carboxyl groups of glutamic and aspartic acids. Hexavalent chromium is probably reduced in biological systems; thus, the prevalent interacting species would be trivalent chromium. Complexes of trivalent chromium with several organic acids (Krebs cycle acids) are known.

Several analytical techniques are sufficiently sensitive to detect chromium concentrations in the parts per billion range in a variety of samples (Section 2.3). Care in handling is necessary to avoid severe contamination of the sample. Loss of chromium as a volatile organo-chromium compound has also been suggested but recent careful work has failed to demonstrate losses from this source.

Chromium can be collected from air by impingers, electrostatic precipitators, and filters (Section 2.3.2). Water samples are collected in containers which do not contain chromium (borosilicate, clean quartz, or polyethylene); the water is acidified and then used for analysis. Inorganic solids are solubilized (ignition, acid digestion, or alkali digestion) before analysis. Biological samples need to be ashed carefully to avoid the possibility of chromium loss. In samples with low chromium content, separation and concentration may be necessary before analysis. Precipitation with hydroxyquinoline and tannic acid may be used. Oxidation in a basic medium forms soluble chromates, whereas many trace elements will precipitate.

Liquid-liquid solvent extraction with the complexing agent ammonium pyrrolidinedithiocarbamate and the solvent methyl isobutyl ketone can concentrate the chromium sample. Prior oxidation of all chromium(III) to chromium(VI) is necessary because this technique extracts only hexavalent chromium. Chromatography can be used to separate chromium from some interfering elements and to concentrate chromium in the sample.

Atomic absorption spectrometry (flame and flameless) is the most common method used to detect chromium in samples (detection limits of about 20 ppb in the flame method and of about 0.2 ppb in the flameless method) (Section 2.3.2.3). With biological samples, the organically complexed chromium should first be converted to inorganic chromium by low-temperature ashing. The flameless atomic absorption method may become more useful for routine, practical analysis in the near future.

Neutron activation analysis is also widely used to determine chromium concentrations, but this method is expensive and is best suited for multielement determinations. After prior treatment to separate and concentrate the element, concentrations of a few parts per billion can be detected. Molecular absorption spectrophotometry, which uses the diphenylcarbazide complex, is a classical analytical method; however, atomic absorption, neutron activation analysis, and emission spectroscopy are now more commonly used. Emission spectroscopy can detect chromium concentrations down to 0.3 ppb and spark-source mass spectrometry can detect about 0.02 to 0.1 ppb. The precision and accuracy of spark-source mass spectrometry can be increased by combining it with the isotope dilution technique. Other methods of chromium analysis include x-ray fluorescence, gas chromatography—mass spectrometry, and single-sweep polarography. These analytical methods, however, are not used extensively.

The greatest problem with chromium analysis, and indeed with chromium studies in general, is the large uncertainty in the analysis of some types of biological and environmental samples. Differences of more than an order of magnitude in the chromium content of NBS bovine liver have been reported by collaborating laboratories and the differences have persisted in spite of considerable time and effort in trying to resolve them. Quite recently, some progress toward getting better interlaboratory agreement has been made, but the reasons for the earlier disagreements remain obscure. Until more is learned about the reasons for the analytical problems, extreme care must be used when drawing conclusions from past analytical results.

1.1.2 Environmental Occurrence

Environmentally, chromium is ubiquitous. Low concentrations (about 10 ppm) are present in granite and limestones, while extremely high concentrations (average about 1800 ppm) are found in ultramafic and serpentine materials (Section 7.2). Chromite is the major mineral form of chromium; all chromium and chromium compounds prepared in the United States are from imported chromite ores. Importation is considerably more economical than mining the U.S. chromite deposits, most of which have a low chromium content. About 75% of the imported ore comes from the U.S.S.R. and South Africa.

Sources of atmospheric chromium include emissions from coal-fired power plants, iron and steel industries, municipal incinerators, and cooling towers. Yearly average concentrations of chromium in urban air (1968 and 1969) ranged from below detection level to 0.1 $\mu g/m^3$; concentrations exceeded 0.1 $\mu g/m^3$ in only 59 of 186 urban cities. Air from nonurban areas did not contain measurable amounts of chromium. Seasonal and day-to-day variations in the amounts of chromium in the air can be expected. Background levels of chromium in air are difficult to determine; a concentration of 5.3 pg/m^3 detected at the South Pole was attributed to weathering of crustal materials.

Most chromium in the atmosphere is particulate. The form of chromium in these particulates is unknown but most likely is the trivalent state. Chromates, however, do occur in the drift from cooling towers. Chromium is present in particulates of all sizes. Although there are conflicting data, smaller particles of fly ash from coal combustion generally have somewhat higher chromium concentrations than larger particles. The data suggest that surface enrichment of particulates may occur during the combustion process.

Chromium concentrations in most soils range from 5 to 300 ppm (Section 7.3.3). The chromium concentration can be considerably higher in soils formed over serpentine rock (500 to 62,000 ppm, ash wt basis). The clay fraction of most soils typically has a higher proportion of chromium. Chromium concentration does not change significantly with depth. Chromium in soils, even those derived from serpentine strata, is mainly in an insoluble state in adsorbed, mineral, or precipitated form. The relative contributions of adsorption to clays, organic matter, and iron or manganese hydrous oxides and of precipitation reactions in decreasing the soluble chromium content are not known. Presumably, these factors would vary with the physical and chemical characteristics of the soil. In most cases, these reactions make chromium relatively unavailable for uptake by plants. Water-extractable chromium in soils is usually less than 0.01 ppm. Chromium amounts extractable by 2.5% acetic acid are likewise low — about 1 ppm in many soils.

Chromium content in soils decreases with distance away from cooling towers. In one study, background levels were reached at about 300 m from the tower. Although chromium in the cooling-tower drift was in the form of chromate, the amount of extractable chromium in the soils was quite low (0.4 to 1.9 ppm). These findings suggest that reduction occurs in the soil and that trivalent chromium is readily adsorbed or precipitated.

Trace quantities of chromium can be found in both surface water and groundwaters. Dissolved chromium concentrations in fresh water ranged from about 0 to 112 ppb, with an average of 9.7 ppb (Section 7.3.4). Higher concentrations were observed in more industrialized areas. Concentrations of chromium were considerably lower in seawater (0 to 0.5 ppb) than in fresh water. In the early 1960s, most waters used as sources of drinking water contained less than 8 ppb chromium. Only 4 of 969 public water supply systems examined in 1969 had finished drinking waters which contained more than 50 ppb chromium.

Electroplating and metal finishing account for the major release of chromium to wastewaters (Section 7.3.4). In addition, the textile and tanning industries release some chromium. Significant amounts can also be contributed by runoff from urban and residential areas (about 9% of the total chromium received at sewage plants in New York City). Relative contributions from different pollution sources to the total amount of chromium found in wastewaters have not been reported for most cities.

In water with little organic matter, both trivalent and hexavalent chromium can exist. Both forms are also found in seawater, but hexavalent chromium is usually the major species (Section 7.3.4).

Significant amounts of chromium occur in particulate form in water. For example, 67.6% of the total chromium in the Walker Branch Watershed (Tennessee) was in particulate form. Chromium concentrations in the suspended particles varied considerably (from 37 to 2000 ppm).

Most sediments contain chromium. Chromium concentrations of 90 to 140 ppm in some California basin sediments and of 1 to 49 ppm in Wisconsin lake sediments were reported (Section 7.3.5). Concentrations of up to 1240 ppm chromium have been found (Rhine River sediments). Slightly higher chromium concentrations were reported in surface sediments. Although anthropogenic input of chromium occurs, the amount has not been great enough to cause large surface concentrations in sediments from most areas.

1.1.3 Environmental Cycling and Fate

Although some aspects of the environmental cycling of chromium are known, quantitative data on the amount cycled are lacking (Section 7.4). Atmospheric chromium, mainly in particulate form, is deposited on land or water by fallout and precipitation (Section 7.4.1). Chromium concentrations in rain ranged from 0.6 to 60 ppb; a monthly deposition of 11 g of chromium per hectare was reported.

Chromium in the soil is rather immobile. It is mainly in the trivalent state because hexavalent chromium is reduced in the presence of organic matter (Section 7.4.2). Little information on chromium loss by leaching and surface runoff exists. Anaerobic conditions in some soils may slightly enhance chromium solubility. Weathering and wind action probably contribute a small amount of chromium to the atmosphere, but this amount has not been quantified.

Flowing water transports vast amounts of chromium (for example, 790 metric tons per year by the Susquehanna River). In one study, most chromium was found to be transported in the form of crystalline sediments. Existing data suggest that mobilization of chromium from sediments to soluble form does not occur when the suspended material of a river is deposited in an estuary. In water, hexavalent chromium is effectively adsorbed and precipitated with $MnO_2 \cdot nH_2O$ but not with $Fe_2O_3 \cdot nH_2O$, apatite, or clay. The relative amounts of chromium supplied to many basins by various sources, such as wind, sewer outfalls, storms, runoff, and river flow, have not been determined.

Little information is available on the fate of chromium in sediments. Currents determine the pattern of sediment deposition. Storms and other violent weather could stir sediments, especially in shallow areas, and redistribute the chromium within the sediments. Probably, little chromium is recycled. Chelating agents, such as nitrilotriacetic acid used in detergents, are released to the environment and may occur in concentrations which would serve to solubilize metals. However, present data suggest that little chromium is solubilized in this way.

Waste management of chromium in water usually involves reduction of any hexavalent chromium to trivalent chromium followed by precipitation at alkaline pH (Section 7.5). The precipitate is normally disposed of as landfill. Care must be taken to avoid acidification of these landfill sites since chromium (and other metals) would be solubilized. Ion exchange, ion flotation, electrochemical conversion, activated carbon adsorption, liquid-liquid extraction, and reverse osmosis processes are potential waste treatments for chromium removal, but none of these methods are economically practical at present.

The efficiency of chromium removal from sewage varies with treatment plant design and discharge procedure. Overall removal efficiencies of 17% to 18% were reported in one study. Sewage sludge has a wide range of chromium concentrations (20 to 40,000 ppm), most of which is insoluble. Moderate deposition of sewage sludge on land only slightly increases the available chromium content of the soil.

1.1.4 Biological Aspects in Microorganisms

Because of the ubiquity of chromium in the environment, all organisms are exposed to chromium and chromium has been found in all organisms examined. Chromium has not been shown to be an essential element for microbes (Section 3.2). Most microbes take up chromium and those examined contained up to a few parts per million. Microorganisms near pollution sources may contain higher concentrations. Mechanisms of uptake have not been adequately studied; chromate uptake in *Neurospora* is by the sulfate transport system.

Growth inhibition is the major effect observed for chromium additions to growth media (Section 3.3). Different species exhibit different tolerances for chromium. In some cases, other trace elements can overcome the growth inhibition of a specific chromium concentration. Chromium inhibition of photosynthesis has been observed in some algae; inhibition of germination in fungi has also been observed. Chromium inhibits nitrogen fixation in *Azotobacter*. Hexavalent chromium reportedly is mutagenic to *Escherichia coli*.

1.1.5 Biological Aspects in Plants

Considerably more information is available on the metabolism and effects of chromium in higher plants. Although some reports show chromium to be beneficial to plant growth, it has not been found to be an essential element for higher plants (Section 4.2.1).

Plants take up chromium mainly from the soil (Section 4.2.2). Translocation of chromium, supplied as either trivalent or hexavalent chromium, from roots to aerial portions of the plant is small; thus, the highest chromium concentrations occur in roots. If chromium is supplied as the chelate, large amounts are translocated; however, the role of natural chelates within soil in supplying chromium to plants is unknown (Section 4.2.3). Generally, the concentration of chromium within the plant increases as the external available chromium concentration increases.

Chromium concentrations in plants growing on most soils are usually only a few parts per million (Section 4.2.4). However, some plants growing on infertile serpentine soils contain much higher chromium concentrations. The endemic species of physiological races living in serpentine areas seem either to exclude chromium or to tolerate high chromium levels in tissues. The infertility of serpentine soils does not seem to be directly due to the chromium concentration, although it may be a contributing factor. Plants growing on soils amended with sewage sludge have slightly higher chromium concentrations than control plants. These concentrations of chromium apparently produce no toxic effects in the plants.

In solution and pot experiments, excess chromium in the growth medium decreases both shoot and root growth and inhibits seed germination (Section 4.3.2). Growth inhibition can occur at concentrations of less than 1 ppm; at higher concentrations death can occur. Growth inhibition takes the form of decreased size, stunted roots and shoots, or abnormal inflorescence development. Chlorosis occurs in some species.

The symptoms produced by excess chromium and the concentrations which induce them are species specific. Interacting factors such as the content of other elements in the medium can affect the results. Such data are sparse for chromium interactions and plant growth. No data are available on the effects of chromium on cellular metabolism or on how these effects interact to produce the physiological effects observed.

1.1.6 Biological Aspects in Wild and Domestic Animals

Chromium uptake by animals is most easily studied in aquatic species. Both hexavalent and trivalent chromium are taken up by aquatic organisms (Section 5.2.1). Trivalent chromium in waters is often in particulate form and can be ingested; therefore, it is found in the digestive tract of bottom dwellers. Hexavalent chromium compounds are soluble and can be rapidly sorbed by the gut and body walls. Surface adsorption of particulates can occur on shells, gills, mantle, and other body surfaces. Chromium uptake has been demonstrated in clams, polychaete worms, oysters, crabs, and fishes. The effects of high chromium concentrations on these animals include reduced growth and weight, increased oxygen consumption, and increased hematocrits. Both trivalent and hexavalent compounds can be toxic to organisms. In aquatic organisms, toxicity varies with pH, water hardness, temperature, species, and size of the organism (Section 5.3.2). The lethal level of chromium reported for some aquatic invertebrates was approximately 0.05 ppm; for other organisms, lethal concentrations were greater. In soft water, trivalent chromium is more lethal to fish than hexavalent chromium, but in hard water the opposite appears true. Toxic concentrations of chromium vary considerably among different species of fish. For example, median tolerance limits for trivalent chromium in soft water at 24 hr were 4 ppm for guppies, 11 ppm for goldfish, 67 ppm for bluegills, and 5 ppb for fatheads. Values at 48 and 96 hr did not differ greatly. Various insects have reportedly survived exposure to chromium concentrations in the 1 to 64 ppm range. No data were found for chromium interactions in birds, amphibians, or wild and domestic mammals.

1.1.7 Biological Aspects in Humans and Test Animals

Chromium is an essential trace element for humans. Most chromium is taken up by ingestion; lesser amounts are taken up by the respiratory tract and through damaged skin (Section 6.2.1). Absorption can occur through the gastrointestinal and respiratory tracts. Natural chromium complexes, such as the glucose tolerance factor, are absorbed to a greater extent than inorganic trivalent chromium. Hexavalent chromium is reduced to trivalent chromium by acid gastric juices. Inhaled chromium can be trapped in the bronchi and subsequently swallowed (ingested), deposited in the alveoli where it may remain in insoluble form (trivalent compounds), or absorbed into the bloodstream (for example, chromates). Chromium complexes with plasma proteins (β-globulins) of the blood and is distributed to body tissues (Section 6.2.2).

The tissue uptake of chromium administered experimentally depends on the chemical form. Soluble complexes such as acetate and citrate are excreted before much uptake can occur. Compounds which give rise to colloidal or protein-bound forms, such as chromite and chromic chloride, are retained longer and uptake is greater. Phagocytosis of colloidal particles probably explains the uptake of chromite by the reticuloendothelial system, liver, spleen, and bone. Chromium as chromic chloride is also taken up by these organs and accumulates in the spleen. The fetus has an affinity for chromium which may result in marginal chromium deficiency in the mother. The chromium level in the fetus starts to rise during the third month of pregnancy and reaches a peak in the seventh month. In the newborn, the level of chromium decreases. Chromium transferred across the placenta must be in the form of the glucose tolerance factor.

Simple chromium complexes administered in drinking water (5 ppm) increased the chromium levels in the heart, lung, and kidney of test animals (Section 6.2.3.1). Intravenous injection of tracer amounts of chromium as chromic chloride showed that tissue uptake and retention differed among organs. At four days after injection, heart, lung, pancreas, and brain showed a decrease in labeled chromium, whereas spleen, kidney, testis, and epididymis concentrated the labeled chromium.

Adult human tissues generally contain about 0.02 to 0.04 ppm chromium. Lung tissue contains about 0.22 ppm chromium, urine about 1.8 to 11 ppb, and hair about 0.69 ppm. Reports of chromium in blood plasma vary considerably (2 to 520 ppb). Chromium has the greatest affinity for the reticuloendothelial system, spleen, liver, and bone marrow. Hair of newborn humans has a higher chromium content than that of older children. Some organs of

Americans contain less chromium than corresponding organs of people from other nations, which suggests that Americans have a chromium deficiency. Except for the lungs, chromium levels in tissues decrease with age.

Individuals are exposed to chromium mainly through the diet. In humans, daily chromium intake ranges from 5 to 115 ug (Sections 6.3.2 and 8.3). No significant relationship exists between biologically active chromium and total chromium content in foods; thus, certain foods are better sources of available chromium (brewer's yeast, meats, grain, and seafoods). Diets in the United States are often low in chromium as a result of the refinement of most foods.

Elimination of chromium from rats showed three half-lives (0.5, 5.9, and 83.4 days); in humans, overall elimination is slow (Section 6.2.5). Chromium is excreted mainly through urine, although some may be eliminated through feces. About 7 to 15 μg of chromium is excreted daily by humans. In many cases, this amount may be more than is taken in, which results in a slow drain of chromium reserves.

From a biochemical viewpoint, chromium interacts with a variety of ligands; the best-known interaction with proteins is that with collagen during the tanning process (Section 6.2.4). Chromium inhibits some enzymes (for example, β-glucuronidase), but stimulates others. It is an essential component of the glucose tolerance factor. Chromium can also form complexes with nucleic acids, but their biological significance is unknown.

The major role of chromium in metabolism is as a part of the glucose tolerance factor. This complex, which is necessary for normal glucose metabolism, acts by potentiating the action of insulin. Altered tolerance to glucose is the first indication of a deficiency of the glucose tolerance factor and of chromium. Glucose fails to enter the cells because of a lack of the combined action of the factor and insulin. Irreversible metabolic damage may result from long-standing chromium deficiency. The relationship of chromium to diabetes is uncertain, but increased chromium supply has increased glucose tolerance in some diabetics. Lipid metabolism is also altered with chromium deficiency; serum cholesterol levels are higher in chromium-deficient rats and humans. Atherosclerosis is less evident in areas of the world where the population has higher chromium levels. Chromium deficiency also decreases amino acid incorporation into proteins. Chromium deficiency is widespread enough that supplementation with glucose tolerance factor has been suggested as a public health measure.

Chromium is not considered particularly toxic; the amount of chromium needed to produce toxic symptoms is many times higher than the amount needed to relieve symptoms of deficiency. Due to insolubility, trivalent chromium compounds are almost nontoxic when given orally. Hexavalent chromium compounds are strong oxidizing agents and are highly irritating to tissues. They are also easily absorbed and cross cell barriers easily and are therefore more of a toxicity hazard than are trivalent chromium compounds.

Chromium toxicity, which is mainly a problem of occupational exposure, occurs most often with workers directly exposed to dusts or mists of hexavalent chromium compounds. Workers exposed to chromates may develop primary irritations with ulcers and nonulcerative contact dermatitis (eczematous and noneczematous). Duration of contact, susceptibility, and hygiene affect the incidence and extent of these maladies. Improved working conditions can decrease the incidence of skin effects. Treatment with ascorbic acid to reduce hexavalent chromium aids healing of skin irritations.

The major respiratory effects caused by exposure to chromatic dusts or chromic acid mists are ulceration and perforation of the nasal septum. An increased incidence of lung cancer is associated with long-term exposure to hexavalent chromium (Section 6.3.3.2.2). The latent period between first exposure and occurrence of cancer generally appears to be between 10 and 20 years. Dose-response curves for lung cancer are not known. Exposure to chromium compounds for relatively brief periods (days to weeks) can also cause sneezing, rhinorrhea, redness of the throat, bronchospasm, headaches, and dyspnea. Chronic exposure and incidents of high exposure can cause systemic poisoning and result in liver and kidney damage.

In experimental animals, carcinomas, mainly sarcomas, have been produced at the site of implantation of chromium compounds; however, the incidence of occurrence has not allowed a dose-response relationship to be established. No data suggest that chromium poses any mutagenic or teratogenic risk.

The maximum workplace concentration of airborne carcinogenic chromium(VI) recently recommended by the National Institute for Occupational Safety and Health is 1 $\mu g/m^3$ of breathing zone air. Air quality standards for the general population can be expected to be more stringent because the exposure periods are longer and because the population has a wider age variation and range of health complications.

1.1.8 Food Web Interactions

Although some organisms apparently concentrate chromium, no biomagnification in food chains has been observed (Section 8.4). Aquatic ecosystems have been better studied than terrestrial ecosystems. The existing data from both ecosystems indicate that organisms at lower trophic levels contain higher chromium concentrations than organisms at higher trophic levels. The explanation may be that hexavalent chromium absorbed by lower forms is reduced in situ to the less soluble trivalent form, which is not subsequently absorbed by the predator.

1.2 CONCLUSIONS

1. The environmentally important oxidation states of chromium are the trivalent and hexavalent forms. Organic matter reduces hexavalent to trivalent chromium.

2. With suitable analytical procedures, chromium concentrations of less than 1 ppb can be detected. However, continued poor results from

interlaboratory comparison studies indicate that extreme caution should be used when drawing conclusions which depend on the accuracy of analytical results.

3. Major atmospheric emissions of chromium are from the chromium alloy and metal-producing industries; lesser amounts come from coal combustion and cement production. Major emissions to water occur from the electroplating industry.

4. Chromium is ubiquitous in soils and is typically present in the range of 5 to 300 ppm. Most soil chromium is unavailable for plant uptake.

5. Data on the amounts of chromium cycled by environmental factors are lacking. Little chromium is leached from soils; chromium in waters is deposited in sediments.

6. All organisms contain measurable amounts of chromium. Uptake of both trivalent and hexavalent chromium can occur.

7. Mammals appear to be the only group of organisms for which chromium is an essential element.

8. Chromium can reduce both root and shoot growth in plants and can inhibit photosynthesis and nitrogen fixation in microbes. Various organisms have different tolerances and no specific mechanisms of action are known.

9. Chromium is acquired by humans mainly through ingestion and distributed to tissues by the blood.

10. Altered glucose tolerance is the first observed symptom of chromium deficiency. Chromium is involved in glucose metabolism as part of the glucose tolerance factor, which acts with insulin to govern the entry into cells of sugars as well as amino acids and lipids.

11. Diets in the United States are often low in chromium as a result of the refinement of many foods. Some evidence suggests a deficiency of chromium and of the glucose tolerance factor which becomes more severe with age.

12. Chromium toxicity is mainly an occupational concern. Trivalent chro[illegible] compounds are not a great toxicity hazard. Industrial exposure [illegible] dusts or mists of hexavalent chromium compounds produces dermatitis, skin lesions, and ulceration and perforation of the nasal septum. Systemic effects may also result. With long-term exposure, the incidence of lung cancer increases.

13. No biomagnification of chromium has been observed in organisms of a food chain. Chromium concentrations are highest in members of the lower trophic levels.

14. Probably the greatest single concern in drawing conclusions on chromium effects in the environment is the analytical uncertainty shown by interlaboratory comparison data. Drawing firm conclusions in the face of these unresolved problems can be quite hazardous.

SECTION 2

PHYSICAL AND CHEMICAL PROPERTIES AND ANALYSIS

2.1 SUMMARY

The inorganic chemistry of chromium has been well studied and understood. However, its biologic and environmental interactions are obscure and poorly characterized. This dichotomy is the direct result of the chemical complexity of the element and the extremely low chromium concentrations often found in living matter. Chromium occurs in valence states ranging from -2 to +6. The tripositive state, the most stable form, exhibits a very strong tendency to form six-coordinate octahedral complexes with a great variety of ligands such as water, ammonia, urea, halides, sulfates, ethylenediamine, and organic acids. In neutral and basic solutions, trivalent chromium forms polynuclear compounds in which adjacent chromium atoms are linked through OH or O bridges. These compounds may eventually precipitate as $Cr_2O_3 \cdot nH_2O$. Hexavalent chromium compounds have the greatest economic importance as well as biological and environmental significance. All stable hexavalent chromium compounds are oxy species (such as CrO_3, CrO_4^{2-}, and CrO_2Cl_2) which strongly oxidize organic matter on contact. The other valence states of chromium are too unstable to be significantly involved in the biochemical process with the possible exception of the very stable zero-valent state of "sandwich" complexes, such as dibenzene chromium. There is no evidence that such compounds occur in biologic media.

A variety of analytical techniques is available for the determination of chromium in environmental samples down to the parts per billion level. Although this sensitivity is adequate for most inorganic samples, it can sometimes be achieved only at the expense of costly and time-consuming preanalysis steps. There is a continuing need for more rapid and inexpensive methods of analysis which do not require pretreatment of samples.

The analysis of chromium in organic media is the most serious problem currently confronting researchers interested in the biochemistry of this element. Sometimes present only at the parts per billion level, chromium in organic media is subject to severe contamination from equipment such as knives, needles, and containers. Moreover, there is now little doubt that chromium naturally present in some biological materials behaves differently from inorganic chromium and that it may not be detected by flameless atomic absorption spectrometry when it is introduced directly into the graphite atomizer. The discovery of this disparate behavior of organically bound chromium has rendered suspect much previously reported quantitative data, particularly data defining characteristic levels of chromium in various biological media. Some workers have suggested that the behavior is due to volatile forms of chromium which are lost during ashing, but recent careful attempts to demonstrate volatile chromium species failed. Confidence will be restored to this area of research only when causes of the anomalies are identified and previous assays are verified or amended by new analyses which are beyond suspicion.

2.2 PHYSICAL AND CHEMICAL PROPERTIES

Chromium has been known for more than 175 years and has been an item of commerce during most of this time. Despite this long history, however, many aspects of the element and its interactions with man and the environment remain obscure. Thus, although our knowledge of the inorganic chemistry of simple chromium compounds is well established, our understanding of the biochemistry of chromium is, at best, only rudimentary. This circumstance arises partly from the chemical complexity of the element itself and also from the low concentrations in which it is normally encountered in biological media (Mertz, 1969). A similar lack of information exists concerning the cycling of chromium in the environment (National Academy of Sciences, 1974, p. 108).

In view of the state of the art, this section will necessarily deal chiefly with the inorganic chemistry of chromium; characteristic reactions useful in understanding the behavior of the element will be stressed. However, interactions of biological and environmental relevance will be discussed as fully as existing data permit.

2.2.1 The Element

Chromium was discovered in 1797 by Louis Vauquelin, a French chemist, in the red Siberian ore, crocoite ($PbCrO_4$). The production of chromium chemicals on a commercial basis started soon afterwards in 1816 and has continued without interruption. Chromium compounds now have great economic importance in the paint and dye industries as pigments and mordants, in metallurgy for the production of stainless steel and other alloys, in the chrome tanning of leather goods, in the production of high-melting refractory materials, and, of course, in chrome plating. The steel gray, lustrous, hard metal melts at 1857 ± 20°C, boils at 2672°C, and has a specific gravity of 7.18 to 7.20 at 20°C (Weast, 1974). There is disagreement in the literature concerning the numerical values of measurements involving high temperatures, such as boiling points and melting points. Such measurements should be accepted with reservation.

As found in nature, chromium is a mixture of four stable isotopes of mass numbers 50, 52, 53, and 54. The natural abundances and thermal neutron cross sections of these isotopes are listed in Table 2.1. Also included in this table are descriptions of the five established radioactive isotopes of chromium. The radioisotope commonly used in tracer work is ^{51}Cr. Commercially available chemical forms of this nuclide include chromium(III) in dilute acid and chromate.

Chromium, the 24th element of the periodic chart, belongs to the first series of transition elements. The electronic configuration of the element is $\{Ar\}3d^5 4s^1$. Oxidation states of chromium range from -2 to +6, but it most commonly occurs in the trivalent and hexavalent forms. Hexavalent chromium compounds have the greatest economic importance and also appear to be the most environmentally and biologically significant forms of chromium. Chemically, the most stable and important state is Cr^{3+}, d^3. In this species chromium has a strong tendency to form octahedral complexes of

Table 2.1. Chromium isotopes

Isotope	Natural abundance (%)	Atomic mass	Lifetime	Mode of decay	Decay energy (MeV)	Thermal neutron capture cross section (b)
Chromium		51.996				3.1 ± 0.2
Cr-48			23 h	Electron capture	1.4	
Cr-49			41.9 m	Electron emission	5.26	
Cr-50	4.31	49.9461				16.0 ± 0.5
Cr-51			27.8 d	Electron capture	0.752	
Cr-52	83.76	51.9405				0.76 ± 0.06
Cr-53	9.55	52.9407				18.2 ± 1.5
Cr-54	2.38	53.9389				380 ± 40
Cr-55			3.5 m	Electron emission	2.59	
Cr-56			5.9 m	Electron emission	1.6	

Source: Adapted from Weast, 1977, p. B-278. Reprinted by permission of the publisher.

coordination number six with ligands such as water, ammonia, urea, ethylenediamine, halides, sulfate, and organic acids. Each t_{2g} level in these complexes is singly occupied, which produces a sort of half-filled shell stability (Cotton and Wilkinson, 1962, p. 567). This arrangement results in extremely slow ligand exchange rates and imparts a pseudostability to the complex, even under conditions in which these complexes are thermodynamically very unstable. Oxidation states lower than chromium(III) are strongly reducing; in aqueous solutions only the divalent state is known. Chromium(V) and chromium(IV) are formed as transient intermediates in the reduction of chromium(VI) solutions. They have no stable solution chemistry because of disproportionation to trivalent and hexavalent chromium; however, a few solid compounds are known. The highest oxidation state, chromium(VI), corresponds to the loss of the total number of $3d$ and $4s$ electrons. Stable compounds of this state exist only in the oxy species, such as CrO_3, CrO_4^{2-}, $Cr_2O_7^{2-}$, and CrO_2Cl_2, which are strongly oxidizing. The strong inclination of hexavalent chromium compounds to be reduced to the trivalent state, particularly by organic materials, and the tendency of the resulting trivalent chromium to form very stable complexes with common biological ligands afford obvious mechanisms by which chromium can interact with the normal biochemistry of man. The physical properties of typical chromium compounds are shown in Table 2.2.

2.2.2 Divalent Chromium

Chromium forms divalent compounds with oxygen, the halogens, sulfur, organic acids, and a number of complexing agents. In aqueous solution and in many of its salts, the chromous ion is bright blue. Its chemical behavior is similar to that of the ferrous ion, except that the tendency to pass from the divalent to the trivalent state is much stronger with chromium than with iron. In fact, chromous ions are among the strongest

Table 2.2. Physical properties of typical chromium compounds

Compound	Formula	Appearance	Crystal system and space group	Density (g/cm^3)	Melting point (°C)	Boiling point (°C)	Solubility
Oxidation state 0							
Chromium carbonyl	$Cr(CO)_6$	Colorless crystals	Orthorhombic, C_{2v}^{9}	1.77_{18}	150 (decomposes) (sealed tube)	151 (decomposes)	Slightly soluble in CCl_4; insoluble in H_2O, $(C_2H_5)_2O$, C_2H_5OH, C_6H_6
Dibenzene-chromium(0)	$(C_6H_6)_2Cr$	Brown crystals	Cubic, $Pa3$	1.519	284–285	Sublimes 150 (vacuum)	Insoluble in H_2O; soluble in C_6H_6
Oxidation state + 1							
Bis(biphenyl)-chromium(I) iodide	$(C_6H_5C_6H_5)_2CrI$	Orange plates		1.617_{16}	178	Decomposes	Soluble in C_2H_5OH, C_5H_5N
Oxidation state +2							
Chromous acetate	$Cr_2(C_2H_3O_2)_4 \cdot 2H_2O$	Red crystals	Monoclinic, $C2/c$	1.79			Slightly soluble in H_2O; soluble in acids
Chromous chloride	$CrCl_2$	White crystals	Tetragonal, D_{4h}^{14}	2.93	815	1120	Soluble in H_2O to blue solution, absorbs O_2
Chromous ammonium sulfate	$CrSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Blue crystals	Monoclinic, C_{2h}^{5}				Soluble in H_2O, absorbs O_2
Oxidation state +3							
Chromic chloride	$CrCl_3$	Bright purple plates	Hexagonal, D_3^3 or ^{5}	2.87_{25}	Sublimes	885	Insoluble in H_2O, soluble in presence of Cr^{2+}
Chromic acetyl-acetonate	$Cr(CH_3COCHCOCH_3)_3$	Red-violet crystals	Monoclinic	1.34	208	345	Insoluble in H_2O; soluble in C_6H_6
Chromic potassium sulfate (chrome alum)	$KCr(SO_4)_2 \cdot 12H_2O$	Deep purple crystals	Cubic, T_h^{6}	1.826_{15}	89 (incongruent)		Soluble in H_2O
Chromic chloride hexahydrate	$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$	Bright green crystals	Triclinic or monoclinic	1.835_{25}	95		Soluble in H_2O, green solution turning green-violet
Chromic chloride hexahydrate	$[Cr(H_2O)_6]Cl_3$	Violet crystals	Rhombohedral, D_{3d}^{6}		90		Soluble in H_2O, violet solution turning green-violet
Chromic oxide	Cr_2O_3	Green powder or crystals	Rhombohedral, D_{3d}^{6}	5.22_{25}	2435	ca. 3000	Insoluble
Oxidation state +4							
Chromium(IV) oxide	CrO_2	Dark-brown or black powder	Tetragonal, D_{4h}^{14}	4.98 (calculated)		Decomposes to Cr_2O_3	Soluble in acids to Cr^{3+} and Cr^{6+}

Table 2.2 (continued)

Compound	Formula	Appearance	Crystal system and space group	Density (g/cm³)	Melting point (°C)	Boiling point (°C)	Solubility
Chromium(IV) chloride	$CrCl_4$		Stable only at high temp			830	
Oxidation state +5							
Barium chromate(V)	$Ba_3(CrO_4)_2$	Black-green crystals	Same as $Ca_3(PO_4)_2$				Slightly decomposes in H_2O; soluble in dilute acids to Cr^{3+} and Cr^{6+}
Oxidation state +6							
Chromium(VI) oxide	CrO_3	Ruby-red crystals	Orthorhombic, C_{2v}^{16}	2.7_{25}	197	Decomposes	Very soluble in H_2O; soluble in CH_3COOH, $(CH_3CO)_2O$
Chromyl chloride	CrO_2Cl_2	Cherry-red liquid		1.9145_{25}	-96.5	115.8	Insoluble in H_2O, hydrolyzes; soluble in CS_2, CCl_4
Ammonium dichromate	$(NH_4)_2Cr_2O_7$	Red-orange crystals	Monoclinic	2.155_{25}	Decomposes 180		Soluble in H_2O
Potassium dichromate	$K_2Cr_2O_7$	Orange-red crystals	Triclinic	2.676_{25}	398	Decomposes	Soluble in H_2O
Sodium dichromate	$Na_2Cr_2O_7{\bullet}2H_2O$	Orange-red crystals	Monoclinic	1.348_{25}	84.6 (incongruent)	Decomposes	Very soluble in H_2O
Potassium chromate	K_2CrO_4	Yellow crystals	Orthorhombic	2.732_{18}	971		Soluble in H_2O
Sodium chromate	Na_2CrO_4	Yellow crystals	Orthorhombic, D_{2h}^{17}	2.723_{25}	792		Soluble in H_2O
Potassium chlorochromate	$KCrO_3Cl$	Orange crystals	Monoclinic	2.497_{39}	Decomposes		Soluble in H_2O, hydrolyzes
Silver chromate	Ag_2CrO_4	Maroon crystals	Monoclinic	5.625_{25}			Very slightly soluble in H_2O; soluble in dilute acids
Barium chromate	$BaCrO_4$	Pale yellow solid	Orthorhombic	4.498_{25}	Decomposes		Very slightly soluble in H_2O; soluble in strong acids
Strontium chromate	$SrCrO_4$	Yellow solid	Monoclinic, C_{2h}^{5}	3.895_{15}	Decomposes		Slightly soluble in H_2O; soluble in dilute acids
Lead chromate	$PbCrO_4$	Yellow solid	Orthorhombic				
		Orange solid	Monoclinic, C_{2h}^{5}	6.12_{15}	844		Practically insoluble in H_2O; soluble in strong acids
		Red solid	Tetragonal				

Source: Adapted from Hartford and Copson, 1964, Table 3, p. 480-481. Reprinted by permission of the publisher.

known reducing agents in aqueous solution; the standard reduction potential for the chromium(II)/chromium(III) couple is -0.4 V (Weast, 1974). Due to this tendency to oxidize, chromous compounds are not found in nature (National Academy of Sciences, 1974, p. 4), nor is there yet any evidence that divalent chromium plays any biochemical role (Schroeder, 1970).

2.2.3 Trivalent Chromium

The trivalent state of chromium is the most stable oxidation state of the element and the most important chemically. The foremost characteristic of this state is the strong tendency to form kinetically inert hexacoordinate complexes. Because of the very slow ligand exchange rate, many of these complexes can be isolated as solids even though they are quite unstable thermodynamically. This characteristic has great relevance in studies of the behavior of chromium(III) in biological systems. In acid solutions, even the simple ion is coordinated with the solvent as $[Cr(OH_2)_6]^{3+}$. The tendency to coordinate is as marked in the trivalent chromium species as in any other known element and extends to all kinds of ligands; it is especially strong with nitrogen compounds such as amines (Sidgwick, 1950, p. 1014).

2.2.3.1 Chromic Oxide — This green, insoluble, crystalline oxide (Cr_2O_3) is formed by burning chromium metal in oxygen, by thermal decomposition of chromium trioxide or ammonium dichromate, or by roasting the hydrous oxide ($Cr_2O_3 \cdot nH_2O$). The latter compound, frequently called chromic hydroxide, is precipitated by addition of hydroxide to solutions of chromium(III) salts (Cotton and Wilkinson, 1962, p. 685). Chromic oxide is insoluble in both acid and base if it is too strongly ignited; otherwise, it and its hydrous form are amphoteric and dissolve readily in acid to yield aquo ions, $[Cr(H_2O)_6]^{3+}$, and in concentrated alkali to give chromite, $[Cr(OH)_4]^-$. Chromic oxide is thermally unstable at elevated temperatures and begins to dissociate near its melting point (about 2275°C).

Chromic oxide is frequently used as a pigment in paint, particularly in painting on glass, porcelain, fabrics, and bank notes (Stecher, 1968). As a pigment, it is identified as Anadomis green, Casalis green, chrome green, chrome achre, chromic oxide green, chromia, green cinnabar, and green rouge (International Agency for Research on Cancer, 1973).

2.2.3.2 Chromic Sulfide — Chromic sulfide (Cr_2S_3) is a green or black crystalline solid whose color depends upon its state of division. It can be made directly from the elements or by various high-temperature reactions, such as the treatment of $CrCl_3$ with H_2S at red heat. It is not formed by precipitation from aqueous solutions due to hydrolysis to $Cr_2O_3 \cdot nH_2O$ and H_2S. Consequently, it does not occur naturally. Chromic sulfide burns in air to the oxide or basic sulfate, but it is very resistant to acids in the cold, being attacked only by nitric acid and aqua regia (Sidgwick, 1950, p. 685).

2.2.3.3 Chromic Halides — Chromium forms trihalides with all four halogens; the first three have been prepared in the anhydrous state and all four are known in one or more hydrated forms. The chlorides are the most important chromium halides. Anhydrous chromic chloride does not dissolve appreciably in cold water, alcohol, acetone, or ether, but it goes into solution readily in the presence of a small amount of chromium(II) ion or a reducing agent such as stannous chloride (Cotton and Wilkinson, 1962, p. 68). Mineral acids, including aqua regia, have no action on the anhydrous chloride salt. Fused alkali hydroxides or carbonates, in the presence of nitrates, react with $CrCl_3$ to form chromates. A considerable number of hydrated chromic chlorides are known. In concentrated solutions above 30°C, the dark green hexahydrate, $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$, is the stable species. This commercial solution is sometimes used as a mordant, in tanning, and in the preparation of chromium complexes. Usually, however, the basic chloride is preferred for these uses (Hartford and Copson, 1964).

The other chromic halides are generally similar to the chloride. Fluoride is used for printing and dyeing woolens, mothproofing woolen fabrics, and coloring marble.

2.2.3.4 Other Simple Salts — Only a few salts are pertinent to this discussion. Anhydrous chromic sulfate, which can be prepared from the oxide with sulfuric acid, has the color of a peach blossom and, like the chromic chloride, is insoluble in water except in the presence of a chromous salt or other reducing agent. It forms a series of green and violet hydrates which contain up to 18 molecules of water (Cotton and Wilkinson, 1962, p. 687). These salts are used extensively in manufacturing paints, varnishes, and inks, as well as frits for coloring porcelain. A deep violet hydrated nitrate, $Cr(NO_3)_3 \cdot 9H_2O$, is used along with several lower hydrates in preparation of chromium catalysts and in textile printing. Upon dehydration, these salts decompose to chromic oxide and oxides of nitrogen. A variety of chromic salts of organic acids are used for printing cotton in skeins and in the experimental tanning of leather.

2.2.3.5 Hexacoordinated Complexes — The most characteristic feature of the solution chemistry of chromium is the pronounced tendency of chromium(III) to form coordination compounds. Literally thousands of these complexes exist and they appear to be always hexacoordinate (Cotton and Wilkinson, 1962, p. 687). Although a large number of chromium complexes are known, they can be classified into a relatively small number of types, as outlined below.

2.2.3.5.1 Ammines — The group of complexes in which chromium is attached to nitrogen is probably the largest and most stable. It includes the pure ammines, $(CrAm_6)^{3+}$; the mixed amine-aquo complexes, $[CrAm_{6-n}(H_2O)_n]^{3+}$ (n = 0 to 4, 6); the mixed amine-acid complexes, $(CrAm_{6-n}X_n)^{(3-n)+}$; and the mixed amine-aquo-acido complexes, $[CrAm_{6-n-m}(H_2O)_nX_m]^{(3-m)+}$, where Am represents the monodentate NH_3 or half of a bidentate amine such as ethylenediamine and X represents a univalent acido ligand such as a halide or nitro ion (Rollinson, 1973, p. 666). Examples of specific complexes which have been prepared are given in Table 2.3.

2.2.3.5.2 Aquo ions — The hexaquo ion, $[Cr(OH_2)_6]^{3+}$, occurs in aqueous solutions of all simple chromic salts and in many of their crystals as well (Cotton and Wilkinson, 1962, p. 687). Among these are the violet hexa-

Table 2.3. Some mononuclear chromium(III) complexes of singly coordinating and bidentate chelating ligands

Type[a]	Ligands[b]
$[CrA_6]^{3+}$	A = H_2O; NH_3; NH_2CONH_2; ½ en; ½ pn; ½ dipy, ½ phen; ½ biguanide
$[CrA_5B]^{3+}$	A, B = NH_3, H_2O
$[CrA_5X]^{2+}$	A, X = H_2O, Cl^-; H_2O, NO_3^-; NH_3, Cl^-; NH_3, Br^-; NH_3, NO_3^-; NH_3, NO_2^-
$[CrA_3B_2X]^{2+}$	A, B, X = NH_3, H_2O, Cl^-; NH_3, H_2O, Br^-
$[CrA_4X_2]^+$	A, X = ½ en, ONO^-; ½ en, Cl^- (*cis*); ½ en, SCN^- (*trans*); ½ dipy, Cl^-; ½ phen, Cl^-; ½ dipy, ½ ox^-; ½ phen, ½ ox^-
$[CrA_3BX_2]^+$	A, B, X = NH_3, H_2O, Cl^-; NH_3, H_2O, Br^-
$[CrA_3X_3]^0$	A, X = H_2O, Cl^-; C_2H_5OH, Cl^-; NH_3, Cl^-; THF, Cl^-; py, Cl^-; *N*-substituted amide, Cl^-
$[Cr(AX)_3]^0$	AX = acac; hfa, 3-bromoacetylacetone; formylacetone; malonaldehyde; glycine; alanine; methionine
$[CrA_2X_4]^-$	A, X = NH_3, SCN^-; $C_2H_5NH_2$, SCN^-; py, SCN^-; H_2O, ½ ox^-; ½ dipy, ½ ox^-; ½ phen, ½ ox^-
$[CrAX_5]^{2-}$	A, X = H_2O, Br^-
$[CrX_6]^{3-}$	X = CN^-; SCN^-; ½ ox^-

[a] A, B = singly coordinating neutral molecule or ½ bidentate chelating neutral molecule; X = singly charged negative ion or ½ bidentate doubly charged chelating ion; AX = bidentate chelating ligand coordinating via one neutral and one negative group.

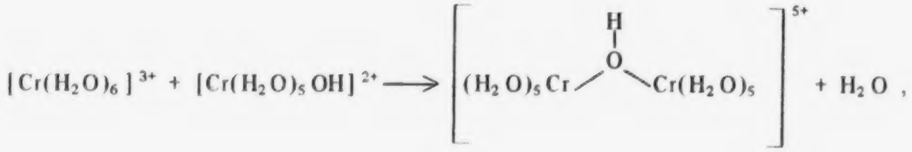
[b] en = ethylenediamine; pn = propylenediamine; dipy = dipyridyl; phen = 1,10-phenanthroline; py = pyridine; acac = acetylacetone; hfa = hexafluoroacetylacetone; THF = tetrahydrofuran; ox = oxalate.

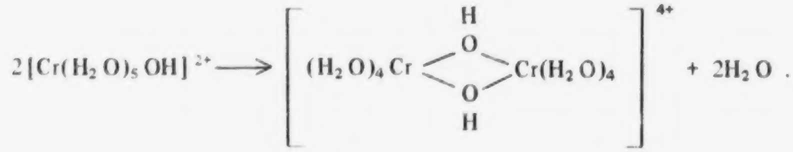
Source: Adapted from Rollinson, 1973, Table 16, p. 667. Reprinted by permission of the publisher.

hydrates of the chloride and the bromide and an extensive series of alums, $M^ICr(SO_4)_2 \cdot 12H_2O$. Examples of mixed aquo-ammine complexes are given in the preceding section.

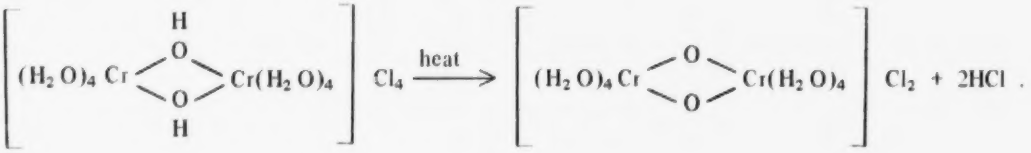
2.2.3.5.3 Acido complexes — Trivalent chromium also forms anionic complexes of the type $(CrX_6)^{3-}$, where X is a monodentate anion such as F^-, Cl^-, CN^-, SCN^- or part of a polydentate anion such as oxalate. As was the case with ammine and aquo complexes, mixed acido-aquo and acido-ammine species also occur. A commonly occurring complex of the latter type is Reinecke's salt, $NH_4[Cr(SCN)_4(NH_3)_2] \cdot H_2O$, which is widely used to precipitate large cations (Kleinberg, Argersinger, and Griswold, 1960, p. 526).

2.2.3.5.4 Polynuclear complexes — In alkaline media, chromium(III) tends to form a variety of polynuclear complexes through olation (Rollinson, 1973):





The diol produced by the second reaction, and any other polynuclear products containing water molecules, can release further hydrogen ions, creating more coordinated OH groups and a higher state of aggregation. Under appropriate conditions, the aggregates may attain colloidal dimensions and ultimately precipitate a three-dimensional olated complex, $Cr(OH)_3 \cdot XH_2O$. This tendency frequently causes difficulties in carrying out reactions in neutral or basic solutions. Olation is favored by heat, increased concentration, increased basicity, and time. Thus, the biological activity of simple chromium complexes may be a function of the age of such solutions, a factor not always given sufficient consideration (Mertz, 1969). If olated compounds are heated sufficiently, still more acid is eliminated and the chromium atoms are then linked through oxygen atoms (oxolation):



Mesmer and Baes (1975) have critically reviewed the hydrolysis behavior of metal-containing cations of a number of metals, including chromium, by applying molecular orbital and ligand field theory. Chromium(VI) is extensively hydrolyzed in water and gives only neutral or anionic species. Chromium(III) compounds can give rise to polymers, as discussed above, which exhibit sluggish kinetic behavior due to the stabilization of this d^3 ion against ligand displacement reactions.

2.2.4 Tetravalent and Pentavalent Chromium

These valence states are irrelevant to the aqueous chemistry of chromium; no stable solutions are known. However, various nonaqueous techniques may be utilized to prepare a limited number of tetravalent and pentavalent chromium compounds.

2.2.5 Hexavalent Chromium

Hexavalent chromium is the highest oxidation state and the second most stable valency, next to that of chromium(III). All stable hexavalent chromium compounds are exclusively oxy molecules and potent oxidizing agents (Cotton and Wilkinson, 1962, p. 689). The hexafluoride (CrF_6) is sometimes cited as an exception to this statement, but this thermally unstable yellow halide decomposes to CrF_5 and F_2 at -100°C (Rollinson, 1973). Hexavalent chromium occurs rarely in nature, apart from man's invention, because it is readily reduced in the presence of organic matter. However, after introduction by man, hexavalent chromium frequently remains unchanged in many natural water sources because of the low concentration of reducing matter. Hexavalent chromium occurs most commonly in the form of chromate or dichromate, both of which are high-tonnage industrial products (National Academy of Sciences, 1974, p. 5).

2.2.5.1 Chromium Trioxide — Chromium trioxide (chromic anhydride, CrO_3) is readily precipitated in the form of bright red needles by the addition of sulfuric acid to aqueous solutions of sodium or potassium dichromates. The trioxide melts at 197°C, but it is unstable at higher temperatures, gradually losing oxygen until Cr_2O_3 is formed. Chromium trioxide is very hygroscopic; its solubility in water as a function of temperature is given in Table 2.4. The trioxide is a very powerful oxidizing agent. Hydrogen, ammonia, and hydrogen sulfide are oxidized in the gaseous state. Certain organic materials such as alcohol or paper are ignited on brief contact with CrO_3 (Udy, 1956, p. 135). Chromic acid (H_2CrO_4 or $CrO_3 \cdot H_2O$), the hydrated form of chromium trioxide, does not occur in the free state, but it is readily formed in solution. Most metals dissolve in chromic acid solutions. Iron, however, soon develops a passivity for further reaction when it is exposed to certain concentrations of the acid. Anodized aluminum is also resistant to oxidation by chromic acid.

Chromium trioxide is widely used in chrome plating and other metal-finishing operations and in recirculating water systems and cooling towers as a corrosion inhibitor for ferrous alloys (International Agency for Research on Cancer, 1973).

2.2.5.2 Chromates, Dichromates, and Polychromates — Sodium chromate and sodium dichromate, primary products of the chemical industry, are produced by roasting chromite ore in the presence of soda ash. The soluble chromates are removed by leaching with water and are converted to sodium dichromate by treatment with sulfuric acid.

All of the metallic chromates, except those of the alkalies and the light alkaline earths, are insoluble in water. As the pH is lowered, solutions of chromate ions turn orange because of the formation of dichromate ions:

$$2CrO_4^{2-} + 2H^+ = Cr_2O_7^{2-} + H_2O, \quad K = 4.2 \times 10^{14}.$$

Acid solutions of dichromate are powerful oxidizing agents:

$$Cr_2O_7^{2-} + 14H^+ + 6\underline{e} = 2Cr^{3+} + 7H_2O, \quad E = 1.33 \text{ V vs SHE}.$$

Table 2.4. Solubility of chromium trioxide and selected chromates in water

Temperature (°C)	Solubility (wt %)						
	Chromium trioxide	Ammonium chromate	Sodium chromate	Potassium chromate	Ammonium dichromate	Sodium dichromate	Potassium dichromate
0	61.70	19.78	24.21	37.14	15.16	70.60	4.3
10	62.08		32.11	38.05	21.06	71.67	7.8
20	62.49		44.36	38.96	26.67	73.16	11.7
30	62.91	28.8	46.84	39.80	31.98	75.00	16.1
40	63.39		48.84	40.61	36.99	77.09	20.9
50	63.90	34.40	51.04	41.40	41.72	79.46	26.0
60	64.46	37.21	53.54	42.15	46.14	82.04	31.3
70	65.08		55.2	42.88	50.27	84.98	36.6
80	65.79		55.5	43.60	54.10	88.39	42.0
90	66.59		55.8	44.31	57.65	90.60	46.5
100	67.46		56.1	45.00	60.89	91.43	50.2

Source: Adapted from Udy, 1956, Tables 6.5 and 6.33, pp. 131, 161-162, Volume I, ACS Monograph No. 132, 1956. Reprinted by permission of the publisher.

Basic solutions of the chromate ion are much less oxidizing:

$$CrO_4^{2-} + 4H_2O + 3\underline{e} = Cr(OH)_3(s) + 5OH^-, \quad E = -0.13 \text{ V vs SHE.}$$

The solubilities of the most important chromates and dichromates are given as a function of temperature in Table 2.4.

Potassium dichromate, once the leading commercial form of chromium, has now been largely replaced by the less costly sodium dichromate, from which almost all other chromium chemicals are prepared. In view of the ubiquity of sodium dichromate, this compound, more than any other, is probably responsible for the pollution of our waterways with hexavalent chromium.

2.2.5.3 Other Compounds — Hexavalent chromium also occurs in several other types of compounds: the halochromates, the chromyl halides, and the peroxychromates. None of these have the chemical or economic importance of the chromates.

2.2.6 Biochemistry of Chromium

Chromium interacts in some manner with a wide assortment of biologically relevant compounds. As discussed later, the chief biochemical function of chromium apparently relates to insulin and the membrane transport of cell metabolites. Insulin requires chromium at the site of action to exert its maximal effect. On the other hand, without insulin, chromium and its complexes are inert. The mechanisms by which these interactions occur are not yet apparent (Mertz, 1969). Chromium also interacts strongly with nucleic acids. Wacker and Vallee (1959) found more than 1000 ppm chromium in a ribonucleoprotein from beef liver. Whether or not this high concentration of chromium associated with ribonucleoprotein has any biochemical significance has not yet been established. Chromium also appears to interact with enzymes, bacteria, yeasts, red blood cells, and a variety of substances with low molecular weight (Mertz, 1969).

The chemistry of these interactions is unknown. Based upon the established inorganic chemistry of trivalent chromium, interaction could be expected to occur by the formation of chromium complexes with oxygen or nitrogen donors in the substrate. This mechanism is known to occur in the chrome tanning of leather. Here, chromium reacts mainly with the free carboxyl groups of the acidic amino acids of the protein (glutamic and aspartic acids), forming stable complexes between different chains of protein (Mertz, 1969). Other binding sites such as hydroxyl groups, peptide bonds, and amino groups probably play only a minor role; masking these does not impair the tanning process appreciably. On the other hand, methylation of the free carboxyl groups prevents tanning completely. Other relevant factors have also been unequivocally established: (1) only trivalent chromium has tanning activity; hexavalent chromium acts only after reduction to the trivalent sites; (2) tanning involves the coordination sites of trivalent chromium; (3) mononuclear trivalent chromium complexes do not tan. The tanning action is initiated by raising the pH of the solution, which causes the formation of olated polynuclear complexes.

These complexes act by accepting carboxyl groups of the collagen strands into their coordination sphere at the expense of previously bound water molecules. Chrome tanning results in nearly total saturation of protein with the metal; various leathers have chromium concentrations of 4% to 6% (Mertz, 1969).

2.2.6.1 Complexes with Biologic Ligands — The fate of chromium ingested into the mammalian system depends on the chemical form and concentration of the chromium species and on the competition for the chromium by hydroxyl ions and other ligands of the biological system. In media of physiological pH, the expected reaction of chromium(III) is olation, except when it is prevented or minimized by competition of ligands other than hydroxyl ions (Rollinson, 1973). One net result of such competition is the establishment of a characteristic state of aggregation of the chromium(III) products for given conditions. This characteristic state of aggregation can be measured by observing the rate of transport of the chromium(III) species through a membrane by the method of sequential dialysis. In this procedure, successive samples of the buffered reaction mixtures are dialyzed at intervals and data are plotted showing the fractional attainment of dialysis equilibrium vs time. The area under the dialysis curve is proportional to the rate of diffusion of chromium(III) and, thus, inversely proportional to the molecular weight of the diffusing species. It is, therefore, a measure of the effectiveness of the ligand in preventing polymerization and, hence, the ligand's coordinating tendency. Measured in this manner, the order of coordinating tendencies of the Krebs-cycle compounds is citrate > isocitrate > malate > oxalacetate > α-ketoglutarate > aconitate > fumarate > succinate. The most effective of the many biological ligands tested are histidine, ATP, ADP, thiamine pyrophosphate, fructose-1, 6-diphosphate, 3-phosphoglycerate, citrate, isocitrate, and tartonate. Glucose does not influence diffusion rates in these experiments, but oleate decreases them strongly, probably through the formation of large, chromium-containing micelles (Rollinson, 1973).

2.2.6.2 Oxidation States — Only trivalent and hexavalent chromium are known to occur in biological media and only the trivalent state is stable in such an environment (Mertz, 1969). The hexavalent form is readily reduced to the trivalent form by a variety of organic species, including tissue in vitro (National Academy of Sciences, 1974, p. 23). There is no evidence that hexavalent chromium may be protected from such reduction by complex formation (Mertz, 1969). Stable "sandwich" complexes in which chromium has a valence of zero have been mentioned as possibly being involved in the binding of chromium to ribonucleic acids (Wacker and Vallee, 1959). However, no experimental evidence exists to support this suggestion.

2.2.7 Environmental Chemistry of Chromium

2.2.7.1 Air — Low atmospheric levels of chromium occur as a result of industrial activity, such as the manufacturing of chromium chemicals, cement, or certain steels. End-product use, such as the burning of coal, paper matches, and fireworks, contributes a share (Schroeder, 1970). Soil-derived aerosols may also be important (John et al., 1973). Chromium air pollution usually occurs as particulate emissions, although mists and sprays may be present at specific locations. Little information exists in the literature regarding the nature of the chemical species present in the atmosphere away from obvious sources of pollution. Sullivan (1969, p. 2) stated that chromium trioxide is perhaps the most important hexavalent compound in the air. This molecule is the anhydride of chromic acid; its chemistry is described in Section 2.2.5. Soil-derived aerosols may contain chromic oxide whose chemistry is treated in Section 2.2.3.1. Further studies are needed to identify other forms of particulate emissions.

2.2.7.2 Water — Chromium appears in some surface waters and in most rivers as hexavalent chromates. Soluble trivalent chromium is not usually encountered in fresh water (Mertz et al., 1974). Seawater contains lower chromium concentrations than the adjoining rivers, apparently because the hexavalent metal is reduced to less soluble trivalent forms which settle to the ocean floor (National Academy of Sciences, 1974, p. 10). About half of the chromium in seawater is thought to be trivalent (Mertz et al., 1974). The chemistry of both trivalent and hexavalent chromium is discussed in Sections 2.2.3 and 2.2.5. Little is known of the aqueous species of chromium present in natural brines.

2.2.7.3 Soil — During weathering, chromium in rocks tends to be oxidized to soluble complex anions (Goldschmidt, 1945). Most soils contain small, varying amounts of chromium (trace to 250 ppm). Very little information is available concerning the chemical form of the element in soils, but it is generally assumed to occur as the trivalent chromic oxide (National Academy of Sciences, 1974, p. 8). Only a small fraction (<1%) of the chromium in soils derived from glacial till can be extracted with acetic acid (Mertz et al., 1974), whereas up to 6% of the total can be extracted from soils derived from bedrock residuum (Taylor et al., 1975). Chromium availability is strongly influenced by the pH of the soil. According to Davis (1956, p. 106), little or no uptake of chromium by plants occurs above pH 4. Therefore, conclusions relative to the availability of chromium in a soil can not be drawn solely on the basis of a total chromium analysis. The chemistry involved in fixing chromium in soils of high pH has not been investigated. However, the fixation chemistry of the six elements adjacent to chromium in the first transition series was studied by Jenne (1968). He concluded that primary fixation occurred by sorption of these heavy metals on the hydrous oxides of manganese and iron, which are commonly present in most soils. Jenne ascribed lesser roles to fixation by organic matter, clays, and carbonates and to precipitation as the discrete oxide or hydroxide. However, Baker (1973) ascribed a more significant role to heavy metal binding by organic matter although he did not present data on chromium.

The chromium content of soils may be greatly increased by repeated applications of phosphate fertilizers and sludges from certain sewage plants. The concentration of chromium in phosphorites from the Idaho-Wyoming-Utah region averages about 1000 ppm (National Academy of Sciences, 1974, p. 9); sludges from selected sewage plants greatly exceed even this concentration (Adams, Eckenfelder, and Goodman, 1973).

2.3 ANALYSIS FOR CHROMIUM

2.3.1 Considerations in Analysis

A variety of methods are available for the determination of chromium in environmental samples. Several of these methods are sufficiently sensitive to detect chromium in the low parts per billion concentration range (Table 2.6). Nevertheless, no one method can be characterized as best for the analysis of chromium in every application; sample load, equipment availability, and cost are key considerations in the method selection. Detection limits, sample matrix, specificity, analysis time, and accuracy must also be considered. These and other factors pertinent to the selection of an analytical method and the evaluation of reported analytical data are summarized in this section.

Although some samples may contain chromium in relatively high concentrations, the element is present at the trace level in most environmental samples. In nutritional research, variations in the concentration of chromium at the nanogram level appear pertinent (Mertz, 1974). At these levels, the accurate analysis of chromium presents a challenge to the analytical chemist which has only recently been solved, if indeed it is solved now. The problem can best be illustrated by interlaboratory comparison data on NBS bovine liver (SRM 1577). Parr (1974) studied this carefully homogenized sample which involved ten laboratories. The results ranged from <0.005 to 1.57 μg/g. Pierce et al. (1976) reported on a study that involved several sample types, including bovine liver. Results from neutron activation analysis, gas liquid chromatography, and flame and furnace atomic absorption were included. Agreement between laboratories and methods was obtained for certain types but not for others. The range for bovine liver was 0.045 to 0.206 μg/g. The existance of volatile forms of chromium was suggested as one possible explanation for the disagreements.

In another study, Greig (1975) compared atomic absorption and neutron activation analysis methods for chromium in marine organisms. Each method was precise but disagreements up to a factor of three existed between methods. Since sample preparation varied with both the method and the organism, the source of the disagreement is hard to establish.

The National Bureau of Standards first issued its bovine liver SRM in 1972. The chromium content has been extensively studied in many laboratories and has only now been established (Dunstan and Garner, 1977). It is soon to be certified at 90 ± 15 ng/g. The existence of this reference material with established chromium values, in addition to the orchard leaves (SRM 1571) and brewer's yeast (SRM 1569), will be of tremendous help in resolving any remaining analytical problems.

In dealing with day-to-day samples containing chromium at the nanogram per gram level, sampling handling techniques assumes greater importance than in ordinary analytical determinations. For example, carefully prepared standards or samples may be invalidated by adsorption of the metal on the container walls or by leaching of contaminants from the container. This problem is obviously aggravated by prolonged storage of such solutions prior to use. Shendrikar and West (1974) studied the adsorption of chromium(III) and chromium(VI) on the walls of Pyrex, flint, and polyethylene beakers as a function of pH and time. Solutions of pH 6.95 initially containing 1 ppm chromium(III) showed negligible losses during the first 24 hr. After this induction period, however, progressive adsorption occurred until 17% to 25% of the element was lost after 15 days. Clearly, neutral or basic solutions of trivalent chromium require acidification prior to storage if adsorption losses are to be avoided. Chromium in the hexavalent state is not appreciably adsorbed under these conditions. In a similar study, Gilbert and Clay (1973) spiked 4 liters of unacidified seawater with 10 μg/liter chromium(III), stored it in a polyethylene bottle, and analyzed 400-ml portions for chromium after 0, 1, 2, 3, 7, and 14 days. The half-life of chromium(III) in solution was only 1.8 ± 0.3 days. Obviously, such samples must be analyzed promptly if serious errors are to be avoided.

The composition of samples can be drastically altered by contaminated reagents used in various preanalysis treatments, such as acidification, dissolution, digestion, and extraction. Care should be taken that only reagents of the highest purity are used; even so, the quantity added should be limited to avoid unnecessary buildup of contaminants. The conventional chromic acid cleaning solution should not be used for equipment in which trace-level chromium samples are to be processed. In most instances, nitric acid is a suitable substitute.

Precautions must also be taken to avoid contamination of trace-level samples by equipment which may contain chromium. Although some authorities stated that biologic tissues may be safely collected by dissection with stainless steel knives and scissors (National Academy of Sciences, 1974, p. 116), other workers reported unacceptable contamination by their use (Webb, Niedermeier, and Griggs, 1973). The use of grinding or homogenizing equipment apparently can introduce chromium as a result of the pressure and heat generated in the grinding process (National Academy of Sciences, 1974, p. 116). Grinding such samples with an agate mortar and pestle is a safer procedure. Versieck and Speecke (1972) observed a threefold increase of chromium in the initial fraction of blood samples taken by venipuncture with disposable needles. Their studies also showed that chromium introduced by taking liver biopsies with a Menghini needle sometimes exceeded the normal chromium concentration in human liver tissue.

Chromium is generally regarded as a nonvolatile element not subject to losses in mild laboratory heating processes. Conflicting data are reported on the existance of highly volatile, and therefore readily lost, organo-chromium compounds in biological samples. Maxia et al. (1972), Mertz (1974), and Masironi, Wolf, and Mertz (1973) all reported significant losses from some samples even at rather low temperatures. However, Jones, Buckley, and Chandler (1975) conducted very careful experiments with ^{51}Cr-labeled brewer's yeast and found no significant volatility loss up to 800°C. Koirtyohann and Hopkins (1976) labeled rat tissues with ^{51}Cr and found no loss on dry ashing except for blood ashed at 700°C. Very recently, Rook and Wolf (1977) conducted very careful experiments with brewer's yeast and reached the conclusion that <1% of the chromium was lost on heating up to 350°C. Also, the fact that the NBS bovine liver is being certified at a value near the low end of the initially reported range indicates that contamination was probably a greater problem than volatility losses in the earlier work. However, until more data are reported, the validity of the laboratory processing technique must be carefully verified for samples which could contain volatile chromium.

2.3.2 Analytical Procedures

2.3.2.1 Sampling and Sample Handling — Since chromium is ubiquitous (Schroeder, 1970), an essential micronutrient for man (Mertz, 1974), and a toxic environmental pollutant (National Academy of Sciences, 1974, p. 17), many kinds of samples are of interest. The principal requirements for each sample class are discussed below.

2.3.2.1.1 Chromium in air — Because of the chemical nature of chromium, gaseous forms in the air are unlikely. Dusts and fumes of chromium compounds may be collected by any method suitable for the collection of other dusts and fumes; impingers, electrostatic precipitators, and filters are commonly used. The National Air Sampling Network uses a high-volume filtration sampler (Sullivan, 1969). Typical filter media include cellulose, polyethylene, polystyrene, and glass. Begnoche and Risby (1976) used a low-volume sampler with porous polymer filters. Analytical "blanks" should be determined for the chosen filter media because some filter media are contaminated with surprisingly large amounts of chromium (Table 2.5). Dams, Rahn, and Winchester (1972) presented additional data for ten frequently used filter materials. Chromic acid mists may be collected in an impinger using water or caustic solutions.

Skogerboe (1974) and Johnson (1974) have reviewed current methods of monitoring trace metal particulates.

Table 2.5. Trace element concentrations in different materials

Material	Concentration (ppb)			
	Zinc	Iron	Cobalt	Chromium
Polyethylene	25	10,600	0.31	19
Borosilicate glass	730	280,000	81	Not measured
Kimwipe tissue	48,800	1,000	24	500
Millipore filter	2,370	330	13	17,600
Double distilled water	1	<0.2	<0.02	2
Double distilled nitric acid	2	1	0.03	13

Source: Adapted from Bhagat et al., 1971, Table IV, p. 2419. Reprinted by permission of the publisher.

2.3.2.1.2 Chromium in environmental waters — The process of sampling environmental waters for chromium is generally complicated and depends on the homogeneity of the water source, the number of locations sampled, the size of the individual sample, and the manner in which the samples are collected. A more representative sample can usually be obtained by collecting several small samples from different parts of the water body than by collecting one large sample at a single point. Brown, Skougstad, and Fishman (1970) discussed this subject extensively. Descriptions of sampling systems are given in *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1971).

2.3.2.1.3 Chromium in inorganic solids — Chromium can sometimes be determined in solids with little or no prior sample preparation (Murrmann, Winters, and Martin, 1971). Frequently, however, the sample must be dissolved before analysis. The method of solubilization must be adapted to the nature of the sample as well as to the method of determination chosen. Three classical procedures are still generally used: ignition, digestion with acid, and digestion with alkali. If a residue remains, it may be solubilized by fusion with sodium carbonate, followed by treatment with 0.5 *M* sulfuric acid or treatment with hydrofluoric acid. Extraction of the chromium into an immiscible organic solvent, such as methyl isobutyl ketone, may be necessary to eliminate interfering elements or to provide increased sensitivity through concentration of the sample. In this event, any trivalent chromium in the aqueous phase is first oxidized to the hexavalent form to ensure complex formation. The oxidation step may be accomplished by treatment of the sample with silver nitrate and potassium peroxydisulfate (Pinta, 1966, p. 277) or with potassium permanganate and sodium azide (Brown, Skougstad, and Fishman, 1970).

2.3.2.1.4 Chromium in biological media — Although the analysis of chromium in many inorganic samples is routine, even at the trace level, serious problems are currently associated with the determination of chromium in biological materials. Mertz (1974) asserted that analysis is the "most difficult and important" problem facing workers in this area of research. He stated that although analyses of chromium obtained by one laboratory in one tissue may be relatively consistent, results obtained by different investigators and efforts to establish "normal" chromium concentrations in various tissues must be viewed with skepticism until the composition and volatility of chromium compounds in organic media are established. These problems are discussed in Section 2.3.1.

2.3.2.2 Separation and Concentration — Environmental samples often contain chromium in such small amounts that concentration or separation from potential contaminants is required. Evaporation is sometimes used as a concentration procedure; however, more specific techniques are usually required to eliminate interfering constituents.

2.3.2.2.1 Precipitation — Chromium can be precipitated from aqueous solutions by a number of reagents; hydroxyquinoline (oxine) and tannic acid are used for this purpose. However, this procedure is not generally recommended for environmental samples containing low chromium concentrations because the risk of loss is great. Another application of precipitation for the separation of chromium involves oxidation in a basic medium, whereby chromate is formed and remains in solution while a great many other metals such as iron, manganese, titanium, nickel, and cobalt are precipitated. The oxidation can be effected in hot solution with sodium peroxide, hydrogen peroxide, and sodium hydroxide or with bromine and sodium hydroxide (Sandell, 1959, p. 388). Methods in which a trace component is to be retained in solution while interferences are precipitated often fail due to coprecipitation of the analyte.

2.3.2.2.2 Solvent extraction — Liquid-liquid solvent extraction is a widely used method for separating and concentrating chromium in environmental samples. This technique can be highly selective and, unlike precipitation, can be used for very small quantities of material (Andelman, 1971). In this method, an immiscible organic solvent is equilibrated with an aqueous solution containing chromium in a complexed state; the phases are then separated and the organic phase, in which the chromium species preferentially concentrates, is used as required, either for further separation and concentration or directly in analysis. The smaller the volume of the extracting solvent, the greater will be the concentration factor. Ammonium pyrrolidinedithiocarbamate is a commonly used complexing agent for chromium extraction (Goulden, Brooksbank, and Ryan, 1973). Typically, methyl isobutyl ketone is used as the organic solvent (Brown, Skougstad, and Fishman, 1970). This technique recovers only hexavalent chromium; if trivalent chromium is to be extracted, it must first be oxidized (Section 2.3.2.1.3). The efficiency of the extraction process should be verified for the concentrations and sample types of interest.

2.3.2.2.3 Chromatographic methods — Trivalent chromium can be separated from iron(III), aluminum, uranium, cerium, titanium, nickel, copper, molybdenum, manganese, cobalt, thorium, zinc, vanadium(V), tungsten, gallium, indium, and thallium by adding excess 8-hydroxyquinaldine to precipitate chromium and most of the other metals, dissolving the dried precipitate in chloroform, diluting this with an equal volume of benzene, and passing the solution through a column of activated alumina. Chromium is eluted with a mixture of chloroform and benzene; the other metals remain on the alumina. In the absence of aluminum, cobalt, and vanadium, 8-hydroxyquinoline can be used as the complexing agent (Sandell, 1959, p. 390). The technique would probably not be applicable to samples at low concentrations. Wolf et al. (1972) used the gas chromatographic technique to concentrate and separate picogram amounts of chromium in human blood plasma and serum.

2.3.2.3 Methods of Analysis — Chromium can be determined by a variety of analytical procedures. Methods which are currently important or show future promise are described in this section. Emphasis is placed on performance and limitations of each procedure rather than on minute details. Table 2.6 lists various instrumental methods for the determination of chromium. Detection limit, precision, accuracy, and optimum concentration ranges of samples vary not only among different methods, but also among various models of particular instruments. The tabulated data are, therefore, representative rather than definitive.

Table 2.6. Instrumental methods for the determination of chromium

Analytical method	Important application	Detection limit	Precision (relative standard deviation/sample size)	Relative error	Interfering substances	Selectivity
Atomic absorption spectroscopy (flameless)	Biologic solids and fluids: tissue, blood, urine; industrial wastewaters	0.2 μg/liter[a]	15% (6 μg/liter)[a]	7% (5 μg/liter)[a]	No interfering substances are reported for samples of urine[a] and blood.[b] Less than 10% interference is observed for Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, F^-, SO_4^{2-}, and PO_4^{3-} in certain industrial wastewaters.[c]	Total chromium is measured.
Atomic absorption spectroscopy (flame)	Fresh and saline waters, industrial waste fluids, dust and sediments, biologic solids and liquids, alloys	0.05 μg/liter[d]	5% (3 μg/liter)[d]	3% (5 μg/liter)[c]	Interfering substances present in the original sample are usually not extracted into the organic solvent.	All of the extracted chromium is measured, but only Cr(VI) is extracted from the original sample unless oxidative pretreatment is used.
Neutron activation analysis	Air pollution particulates, fresh and saline waters, biologic liquids and solids, sediments, metals, foods	Sensitivity varies with sample and processing conditions. Typical sensitivites are: 0.2 ng/g[e] (petroleum), 30 ng/g[f] (environmental samples), 0.2 μg/g[g] (biologic material)	3% (8 ng/g)[e] 6% (5 μg)[i]	25% (100 ng/cu m)[j] (air pollution particulates) 20% (2.4 μg/g)[k] (orchard leaves)	Interference may arise from gamma ray activity from other elements, especially Na-24, Cl-38, K-42, and Mn-56. Bremsstrahlung from P-32 may be troublesome.	Total chromium is measured.
Spectrophotometric	Natural water and industrial waste solutions having 5 to 400 μg/liter hexavalent chromium may be analyzed. Higher concentrations must be reduced by dilution	3 μg/liter[l]	3% (400 μg/liter)[l]	2% (0.4 μg/g)[m]	Iron, vanadium, and mercury may interfere.	This method determines only the hexavalent chromium in solution.

Table 2.6 (continued)

Analytical method	Important application	Detection limit	Precision (relative standard deviation/sample size)	Relative error	Interfering substances	Selectivity
X-ray fluorescence	Atomospheric particulates, geologic materials	2 to 10 μg/g (liver)[n] 1.5 μg/g (coal)[o]	4% (25 μg/g)[o] (coal)	1% to 4% (120 μg/cm^2) (air particulates)[p]	The particle size of the sample and the sample matrix may influence the observed measurements.	Total chromium is determined.
Gas chromatography (electron-capture detection)	Blood, serum, urine, natural water samples	0.03 pg[q]	7%[q]		Excess chelating agent or other electron-capturing constituents in the sample may lead to erroneous results.	Only chromium that is chelated and extracted is measured; other electro-negative substances may elute from the column and be detected at the same time as the Cr chelate.
Gas chromatography (atomic spectroscopic detection)	Blood, serum, orchard leaves	~ 1 ng[r]	<6% (1 ng)[r]	20% (2 μg/g)[r]	No interfering is reported.	Only chromium that is chelated and extracted is detected. Atomic spectroscopic methods of detection are inherently more selective for Cr in complex samples, however.
Gas chromatography (mass spectrometric detection)	Blood plasmas, serum	0.5 pg[s]	9% (10 ng/g)[s]	20% (10 ng/g)[s]	No interferences are reported.	Only chromium that is chelated and extracted is capable of being detected.
Emission spectroscopy (arc)	A wide variety of environmental samples	0.5 ng[t]	19% (0.2 μg/m^3)[t] 6% to 12% (50 μg/liter)[u]	10% to 16% (50 μg/liter)[u]		Total chromium is determined.
Emission spectroscopy – inductively coupled plasma source	A wide variety of biological and environmental samples	0.0003,[v] 0.001[w] μg/ml	~ 5%[w]		No interfering substances are reported.	Total chromium is determined.

Table 2.6 (continued)

Analytical method	Important application	Detection limit	Precision (relative standard deviation/sample size)	Relative error	Interfering substances	Selectivity
Mass spectrometry	A wide variety of solid, liquid, or gaseous samples	0.05-1 μg[x]	20% (photographic)[y] 3% ((electrical)[y] 0.5% (isotope dilution)[y]		Potential interferences may arise from any ion having the same mass/charge ratio as the chromium nuclide.	Total chromium is determined.
Chemiluminescence	Fresh, natural waters	30 ng/liter[z]	12% (2 μg/g)[z] 5% (2.3 μg/g)[aa] (orchard leaves)	5% (2.3 μg/g)[aa] (orchard leaves)	Co(II), Fe(II), and Fe(III) interfere but may be measured by running a blank.[bb]	Only trivalent chromium ion is measured.

Sources:

[a] Schaller et al., 1973.
[b] Environmental Instrumentation Group, 1973a.
[c] Morrow and McElhaney, 1974.
[d] Gilbert and Clay, 1973.
[e] Goulden et al., 1973.
[f] Shah et al., 1970.
[g] Bhagat et al., 1971.
[h] Spyrou et al., 1974.
[i] Harrison et al., 1971.
[j] Dams et al., 1970.
[k] De Geoij et al., 1974.
[l] American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1971.
[m] Sandell, 1959.
[n] Kemp et al., 1974.
[o] Kuhn, 1973.
[p] Jaklevic et al., 1974.
[q] Savory et al., 1969.
[r] Wolf, 1976.
[s] Wolf et al., 1972.
[t] Seeley and Skogerboe, 1974.
[u] Barnard and Fishman, 1973.
[v] Fassel and Kniseley, 1974.
[w] Boumanns and deBoer, 1972.
[x] Elser, 1976.
[y] Ahearn, 1972.
[z] Seitz and Hercules, 1973.
[aa] Li and Hercules, 1974.
[bb] Seitz et al., 1972.

Several of the terms used in Table 2.6 are defined variously in the literature. Detection limit (column 3) denotes the smallest quantity that can be determined reliably by the designated technique or instrument. In most techniques, detection limit is defined as two or three times the standard deviation of blank readings (Kaiser, 1973). The precision of the tabulated methods is stated in terms of the relative standard deviation, that is, the standard deviation of a set of samples expressed as a percentage of the mean. Since precision varies with sample size, this information is also indicated in column 4 of Table 2.6. Data in column 5 indicate results of analyzing samples of known composition such as Bureau of Standards material, synthetic standard samples, or samples prepared by the addition of small, successive increments of the component to be determined (differential addition technique). Accuracy is expressed as the relative error. Literature values for the accuracy of a given method vary widely; only a small number of interlaboratory or interprocedural comparisons are available. Consequently, these data must be used cautiously. The following sections briefly describe the various classes of instrumental methods.

2.3.2.3.1 Atomic absorption spectrometry (flame) — In this method of analysis, a previously prepared sample is injected into an air-acetylene flame through which light of 357.9-nm wavelength is passed. The flame atomizes the sample and light from the lamp is selectively absorbed by chromium atoms in proportion to their concentration in the vapor. A photodetector measures the intensity of the 357.9-nm radiation after its passage through the flame and compares it with the intensity of the original line spectrum emitted by the lamp. The results are usually converted and calibrated to read out directly in concentration values. Variations of the above procedure may be desirable with certain samples. The air-acetylene flame may be replaced with a nitrous oxide—acetylene flame which provides greater sensitivity and freedom from chemical interference.

The sensitivity of this method varies with different combinations of the processing variables mentioned above and with sample type, size, and treatment. For example, the absorption of chromium is suppressed by iron and nickel (Ottaway et al., 1973). If the analysis is performed in a lean flame, this interference can be lessened, but the sensitivity will also be reduced. The interference by iron and nickel does not occur in the nitrous oxide—acetylene flame (U.S. Environmental Protection Agency, 1974). Although chromium is not detected as readily as some metals, good detection limits can be obtained under favorable conditions. Thus, Gilbert and Clay (1973) reported a detection limit of 0.05 μg/liter with an extraction for the determination of chromium in seawater. A more conservative detection limit of 0.02 mg/liter (direct aspiration) is reported in the *Manual of Methods for Chemical Analysis of Water and Wastes* (U.S. Environmental Protection Agency, 1974).

Although many environmental samples can be analyzed by atomic absorption spectrometry without prior preparation, an extraction procedure is recommended for samples containing less than 50 μg/liter chromium. Typically, such samples are extracted with ammonium pyrrolidinedithiocarbamate in methyl ethyl ketone.

In general, the precision and accuracy of atomic absorption analyses using flame spectrophotometry are adequate for most inorganic environmental samples such as fresh and saline waters, industrial wastes, dusts and sediments, and metals. A relative standard deviation of ±5% is commonly reported for specialized samples down to the parts per billion level (Gilbert and Clay, 1973; Goulden, Brooksbank, and Ryan, 1973); recoveries of chromium from spiked samples (accuracy) are reported with similar errors. The average precision reported by multipurpose laboratories is somewhat higher than the above figures: 30% to 60% relative standard deviation for samples containing 7 to 400 μg/liter chromium, with an average relative error of about 10% (U.S. Environmental Protection Agency, 1974).

At present, atomic absorption spectrometry with flame atomization is the most widely used procedure for determining chromium in environmental samples (National Academy of Sciences, 1974, p. 117).

2.3.2.3.2 Atomic absorption spectrometry (flameless) — Flameless atomic absorption spectrometry is a relatively new variation of the previously described method in which the sample is atomized directly in a graphite furnace, carbon rod, or tantalum filament instead of a flame. This innovation frequently results in a tenfold to thousandfold increase in sensitivity for many elements (Environmental Instrumentation Group, 1973b, p. 16) and may eliminate the need for sample preparation in certain sample types. The technique may be used for many types of samples of environmental interest, but it is probably most attractive for the analysis of solid and liquid biological samples since the danger of loss or contamination during sample preparation is reduced. Using this technique, Schaller et al. (1973) reported a detection limit (1% absorption) of 0.2 μg/liter chromium in urine, which corresponds to only 10 pg of the metal in the sample analyzed. Replicate analyses of urine containing 6 μg/liter chromium had a relative standard deviation of ±15% and recovery of chromium from spiked samples averaged 93%. These data reflect favorable developmental laboratory conditions; under the routine conditions customarily found in commercial laboratories greater analytical variance may be expected.

The analysis of chromium by the flameless atomic absorption technique is influenced by a number of factors. Henn (1974) observed a variation in absolute sensitivity as a function of sample volume and ascribed the effect to the manner in which the sample was distributed in the graphite furnace. Schaller et al. (1973) found that the specificity of the method was influenced by smoke and nonspecific absorption during the atomization of urine samples. This difficulty was satisfactorily resolved by modifying the charring procedure to destroy the smoke-causing components. Barnard and Fishman (1973) evaluated the heated graphite atomizer for the routine, practical analysis of water samples and concluded that trace metal analysis of water by direct comparison with aqueous standards is impractical because of matrix interference. However, analysis by combining chelation and solvent extraction with subsequent atomization proved satisfactory. Analysis by the method of standard additions was also acceptable.

Background or nonspecific absorption effects are much more severe in flameless absorption than in flame atomic absorption. Fortunately, all major manufactures offer instruments with automatic simultaneous background correction capability. Flameless atomic absorption done without background correction is automatically suspect.

The uncritical use of the flameless atomic absorption technique to determine chromium in organic matrices was questioned by Masironi, Wolf, and Mertz (1973), Wolf, Mertz, and Masironi (1974), and Mertz (1974). These authors investigated the chromium content of different sugar samples and observed large discrepancies depending on whether the samples were ashed in oxygen plasma at 150°C, in a muffle furnace at 450°C, or in the graphite furnace of the atomic absorption spectrometer at 1000°C. As shown in Table 2.7, ashing in a muffle furnace at 450°C resulted in chromium losses of 52%, 46%, 17%, and 0% for molasses and unrefined, brown, and refined sugar, respectively, as compared to the oxygen plasma procedure. Ashing of the same types of sugar in the graphite furance at 1000°C resulted in losses of 89%, 77%, 52%, and >50%, respectively, as compared to the oxygen plasma method. After extensive additional tests the authors concluded,

> (a) inorganic chromium in a sugar matrix can be determined by direct addition of the sample to the graphite furnace; (b) chromium naturally present in sugar and probably in other food-stuffs and biological materials occurs in an organically bound complex that is lost to detection by atomic absorption upon direct placement of the sample in the graphite furnace, i.e., it behaves differently from inorganic chromium; (c) in order to determine organically bound chromium by graphite furnace atomic absorption, it is necessary to convert it to inorganic chromium by oxygen plasma ashing before introduction of the sample into the furnace.

Table 2.7. Mean chromium content in different types of sugars

Type of sugar	Number of samples	Chromium content (ng/g of sample)[a]		
		Oxygen plasma ashing, 150 C	Muffle furnace ashing, 450 C	Graphite furnace ashing, 1000 C (direct analysis)
Molasses	3	266 ± 50	129 ± 54	29 ± 5
Unrefined	8	162 ± 36	88 ± 20	37 ± 13
Brown	5	64 ± 5	53 ± 8	31 ± 2
Refined	7	20 ± 3	25 ± 3	<10

[a] Values listed are averages of means of multiple determinations of each type ± standard mean error of this average.

Source: Adapted from Wolf, Mertz, and Masironi, 1974, Table III, p. 1039. Reprinted by permission of the publisher.

These observations cast doubt on the validity of many published analyses of chromium in biological materials. At the present state of knowledge, analyzing and cross-checking analyses of this type by different techniques apparently are essential. Low-temperature ashing also appears to be an essential step in the analysis of some biological samples.

2.3.2.3.3 Neutron activation analysis — Neutron activation analysis is one of the most sensitive modern analytical techniques for the determination of trace elements. Samples and known standards are irradiated in a nuclear reactor during which time neutrons are captured by various nuclides in the sample. Usually, the production of radioactive isotopes makes it possible by appropriate measurements to identify the daughter activities and relate them to the parent isotope. By comparison with the activity induced in the standards, the amount of sought isotope can be calculated. The induced activity, and, hence, the sensitivity for determining the parent nuclide, is proportional to the amount of the parent isotope present. Neutron fluxes of 10^{12} to 10^{14} neutrons cm^{-2} sec^{-1} are easily available in modern reactors; thus, for irradiations of reasonable length (a few seconds to a few days) most elements can be determined at levels of 10^{-8} to 10^{-10} g (Fulkerson and Goeller, 1973, p. 436).

The commonly used reaction for chromium activation analysis is $^{50}Cr(n,\gamma)^{51}Cr$. Chromium-50 has a thermal neutron absorption cross section of 17.0 barns and a natural abundance of 4.31% (Robertson and Carpenter, 1974). The resulting ^{51}Cr decays with a half-life of 27.8 days and is usually determined by measuring the intensity of the 320-keV gamma ray.

The minimum chromium concentration which can be detected varies with sample type and processing conditions. The following sensitivites have been reported for samples and analyzed without chemical processing: 0.2 ng/g in petroleum (Shah, Filby, and Haller, 1970), 30 ng/g in fresh water (Bhagat et al., 1971), and 0.2 μg/g in biologic material (Spyrou et al., 1974). Greater sensitivities generally can be achieved for given irradiation conditions if the sample is chemically processed to separate and concentrate the element to be determined. For example, after chemically processing the sample, Robertson and Carpenter (1974) cited a sensitivity of 0.1 ng/g for chromium in river water and 3 ng/liter for seawater. McClendon (1974) reported sensitivities at the parts per billion level for chromium extracted from previously irradiated biological and environmental samples.

The precision and accuracy of neutron activation analyses of chromium also vary with sample type and processing conditions but may be generally characterized as good to excellent for most samples. Relative standard deviations of ±10% have been commonly reported for samples containing chromium in the microgram per gram and nanogram per gram ranges (Harrison et al., 1971; Shah, Filby, and Haller, 1970). The relative error was frequently less than 25% (Dams et al., 1970; De Goeij et al., 1974) and may be less than 5% under favorable conditions (McClendon, 1974).

One distinct advantage of neutron activation analysis is reduced problems due to reagent contamination. Even if chemical processing is required, postirradiation contamination is of no consequence in the final result.

Neutron activation analyses are applicable to many kinds of environmental samples including air pollution particulates, dusts, soils, fresh and marine waters, sediments, biologic liquids and solids, and foods. The samples most often are irradiated without prior chemical treatment. However, the procedure is relatively expensive and is normally used only when a multielement determination is required. Since additional elements are determined at small incremental cost, the average cost per element is low if many elements are assayed. The method has another disadvantage when used for the analysis of chromium. Due to intense x-ray or bremsstrahlung activity from ^{24}Na, ^{38}Cl, ^{42}K, ^{56}Mn, and ^{32}P in many samples, the irradiated sample usually must be cooled several weeks before measuring the chromium concentration. The procedure is thus not amenable to rapid or on-line applications. The lengthy cooling period can be reduced to about 24 hr by chemically separating the offending nuclides from the irradiated chromium (McClendon, 1974).

2.3.2.3.4 Molecular absorption spectrophotometry — This analytical method involves forming colored molecular species which absorb radiation in the visible or near ultraviolet range of the spectrum. The amount of radiation absorbed is compared with a previously obtained calibration plot and is related to the metal concentration by the calibration data. The molecular species used to determine chromium is usually the diphenylcarbazide complex, which is reddish purple in slightly acid solutions (American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1971, p. 156). Photometric measurements at concentrations near 400 μg/liter can be made with a precision of about 30%. Accuracy depends on the promptness of the analysis; spectrophotometric comparisons should be made at least 5 min but not more than 15 min after the reagent is added to the sample (American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1971, p. 158).

The molecular absorption method for determining chromium can be used for natural water samples, industrial waste solutions, and solutions of ores and metals if the concentration of hexavalent chromium is in the range of 5 to 400 μg/liter. The technique was used extensively several years ago; now, however, it has been largely supplanted by more sensitive and convenient techniques such as atomic absorption spectroscopy, nuclear activation analysis, and emission spectroscopy.

2.3.2.3.5 Emission spectroscopy — In emission spectroscopy, prepared samples are excited with a flame, arc, spark, or plasma; the resulting light is dispersed with a monochromator, and the characteristic emission lines of each excited element are recorded electronically or on a photographic plate. The concentration of each element is determined by comparing the density of its emission line with that of an internal or external standard. Sample preparation depends in part on the mode of excitation; in general, samples are dissolved and the liquid is deposited on metal or graphite electrodes which are dried before analysis. Precision and accuracy vary with sample type and chromium concentration; standard reference water samples containing 10 to 50 μg/liter chromium can be determined with an apparent accuracy of ±10% to 16% and a relative precision of ±6% to 12%

(Barnard and Fishman, 1973). Seely and Skogerboe (1974) monitored air containing 0.2 μg/liter chromium with a precision of ±19%. Webb, Niedermeier, and Griggs (1973) observed comparable precision in the analysis of biological tissues, but they found that serious errors were introduced if external reference standards and the unknown samples did not contain similar concentrations of matrix elements.

The above examples illustrate that emission spectroscopy is an attractive procedure for analyzing a variety of environmental samples, especially when multielement analysis is required. Adequate precautions must be taken, however, to eliminate bias from matrix effects (Niedermeier, Griggs, and Webb, 1974).

Emission spectroscopy, using an inductively coupled plasma as a light source, has been studied extensively (Boumans and deBoer, 1972, 1975; Fassel and Kniseley, 1974; Olson, Haas, and Fassel, 1977). Sensitivities down to 0.3 ppb have been reported (Environmental Instrumentation Group, 1973*b*, p. 5) using direct aspiration of sample solutions. Precision and convenience are similar to atomic absorption methods and multielement determinations are readily carried out. Although it has not been adequately tested, plasma emission spectroscopy appears to be very promising for the future.

2.3.2.3.6 Spark-source mass spectrometry — Chromium can be determined by exciting a sample with a radio-frequency spark, followed by spectrometric measurement of the resulting ions according to their mass. The ions of different mass-to-charge ratios describe different radial paths through the magnetic field of the electromagnetic analyzer. As a result, they impinge on different points along the detector, usually a photographic plate. The chromium concentration in the sample is measured by the density of the appropriate spectral line on the photographic plate, as compared to that of an element previously added to the sample in known amount. This technique is applicable to virtually any matrix, but results are only semiquantitative. Typically, the detection limits for chromium are 0.02 to 0.1 μg/g, with a relative standard deviation of ±20% (Environmental Instrumentation Group, 1973*b*, p. 14).

The precision and accuracy of the spark-source mass spectrometric method can be greatly improved by using the isotope dilution technique. In this variation, a known quantity of ^{53}Cr is added to the sample and the whole is refluxed with acid until isotopic equilibrium is achieved. A portion of the solution is then transferred to an electrode and is excited by a radio-frequency spark as previously described. The ratio of ^{52}Cr to ^{53}Cr is determined and compared with that of the initial ^{53}Cr spike. The chromium concentration in the original sample is related to the extent of dilution observed in the spiked sample. Relative errors of 0.5% to 3% are typical for samples containing chromium in concentrations varying from micrograms to picograms (Farrar, 1972). This method was recently used to establish the chromium content of NBS bovine liver (Dunstan and Garner, 1977).

The spark-source mass spectrometric technique is relatively expensive in terms of labor and equipment charges per sample, especially if the isotope dilution procedure is used; consequently, it is rarely the method chosen for chromium unless multielement analyses are required. An exception is the analysis of reference materials, such as bovine liver. When economically justified, the method can be applied to a wide variety of environmental samples, such as atmospheric particulates, natural water samples, industrial waste solutions, fuels, and biologic materials. Care must be taken to avoid mass interferences from polynuclear ions having the same mass to charge ratio as the measured chromium nuclides (Brown and Taylor, 1975).

2.3.2.3.7 X-ray fluorescence — Due to recent development in x-ray sources and instrumentation, energy-dispersive x-ray fluorescence is gaining acceptance as a nondestructive method of simultaneously determining groups of elements in a variety of environmental samples (Environmental Instrumentation Group, 1973*b*, p. 11). In this technique, the sample is irradiated with low-energy x-ray or gamma photons which displace K or L orbital electrons from elements of interest. A series of characteristic x-ray lines are then emitted as the electron defects are filled by electrons from higher orbitals. Typically, silicon solid-state detectors are used in conjunction with multichannel analyzers to record and analyze the resulting spectrum (Jaklevic et al., 1974). The intensity of the fluorescence is related to the concentration of the metal in the sample by comparison with radiation from an internal standard. Sample preparation is important; particle size and shape affect the extent to which the irradiating beam is scattered or absorbed. Also, quantitative measurements of trace elements may be complicated by radiation from surrounding atoms. Solid samples can be pressed into thin wafers to minimize these matrix effects. Liquid samples can be processed directly, provided the metal concentrations of interest are at least 1 μg/g; preanalysis enrichment is required for samples of lower concentration.

The precision and accuracy of the method varies with sample type and concentration level; for orchard leaves containing 2.3 ppm chromium, the relative standard deviation and relative error reported by one laboratory were ±64% and 15%, respectively (Environmental Instrumentation Group, 1973*b*, p. 13). In contrast to these data, Kuhn (1973) reported a relative standard deviation of ±4% for coal samples containing 25 μg/g chromium, and Jaklevic et al. (1974) cited a relative error of 1% to 4% in analyzing samples of air particulates containing 120 μg/cm^2 chromium.

The energy-dispersive x-ray fluorescence technique is not yet in widespread use. It appears to have considerable potential for rapid, multielement analysis of certain environmental samples, particularly those which can have more or less homogeneous surfaces, such as filtered air particulates, solutions, and finely divided solids which can be readily pressed into homogeneous pellets.

2.3.2.3.8 Gas chromatography — Gas chromatography is a method of separation in which the components to be separated are distributed between two phases: a stationary bed of large surface area and a gas which percolates through and along the stationary bed. Typically, the stationary bed is a column filled with a finely divided, inert packing which is evenly coated with a suitable liquid sorbent. Alternatively, the stationary bed may be a 0.01- to 0.02-in. inner diameter column onto which a 0.5-μm layer of liquid phase is coated. These columns are known as "capillary" or "open tubular" columns. Helium, hydrogen, or nitrogen is usually used as the gaseous phase. When a sample is placed into a chromatographic column, the unabsorbed carrier gas moves the sample constituents through the column at a rate determined by the interaction of each constituent with the sorbent. Ideally, since each constituent has a different affinity for the sorbent, each component of the sample leaves the column completely resolved from the other components. The composition of the original sample is determined by identifying and measuring each of these fractions. The chromatographic detector serves to identify sample components, and therefore the particular sample constituents under investigation dictate which type of detector to use.

Chromium can be analyzed by gas chromatography as a volatile metal chelate (Moshier and Sievers, 1965; Guiochon and Pommier, 1973). The general procedure is as follows. The sample is first digested to get the chromium in solution. The chromium is then quantitatively chelated with 1,1,1-trifluoro-2,4-pentanedione to form a thermally stable, volatile chromium(III) complex. This complex is subsequently extracted into an organic solvent (usually benzene or hexane), and an aliqout of this extract is injected into the gas chromatograph. It should be noted that only chromium(III) will form the desired complex; therefore, chromium(VI) is reduced to chromium(III) with sodium sulfite immediately after digestion.

Using this procedure, investigators have determined chromium by gas chromatography with a variety of detectors. Savory, Mushak, and Sunderman (1969) and Savory, Glenn, and Ahlstrom (1972) determined chromium in human serum samples using electron capture detection. The limit of sensitivity was reported to be 0.03 pg of chromium. Electron capture detection has also been used to determine chromium in natural waters at picogram levels (Lovett and Lee, 1976; Gosink, 1976) and physiological levels of chromium(III) in urine (Ryan and Vogt, 1977). Wolf (1976) used atomic absorption detection to determine chromium in NBS SRM 1571 orchard leaves, reporting a detection limit of 1 ng chromium. A specially constructed microwave emission detector was utilized by Black and Sievers (1976) to analyze chromium in blood plasma. The 357.9-nm emission line of chromium was monitored to detect as little as 0.9 pg/μl chromium. Wolf et al. (1972) coupled a mass spectrometer to a gas chromatograph to determine chromium in serum and blood. A detection limit of 0.5 pg was reported with a relative error of 20%.

The gas chromatographic analysis of chromium in a variety of biological and environmental samples is very sensitive. Of the detection methods used, the electron capture method is the least specific and therefore requires a very clean extract. Spectroscopic detection methods respond directly to chromium and appear promising. Gas chromatography, with a mass spectrometer detector, is an extraordinarily sensitive and specific method. The high equipment cost will not allow the method to become popular, but it may find an important application in the analysis of biological materials.

2.3.2.3.9 Polarography — Polarographic techniques have a long and honorable history in analytical chemistry, but they have not been applied extensively to chromium analysis. Two recent variations of the method — single-sweep polarography and differential pulse polarography — hold promise as potentially sensitive and rapid techniques. The single-sweep method was applied to chromium in water (with a detection limit of 0.01 ppm) (Whitnack, 1975). Similar detection capability is shown by the differential pulse method (Crosmun and Mueller, 1975; Neeb, 1974). These methods must be regarded as potentially useful but are currently not popular for chromium analysis.

2.3.2.3.10 Chemiluminescence — Luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) emits light when oxidized by hydrogen perioxide. Oxidation occurs only in basic solution in the presence of certain metal ions which catalyze the reaction. In the presence of excess reagents, the intensity of light emission is proportional to the metal catalyst concentration, a property that can be made the basis for trace metal catalyst analysis. The intrinsic sensitivity of the luminol system to small metal concentrations greatly exceeds that of most analytical procedures. For example, the minimum detectable quantity of trivalent chromium in natural water samples is about 25 pg (Seitz, Suydam, and Hercules, 1972).

Chemiluminescence analyses may be performed in static or flowing systems. A typical flowing system was described in detail by Seitz, Suydam, and Hercules (1972). Normally, an analysis is performed in less than 30 min. The precision and accuracy of the chemiluminescence method are not well documented; however, the available data are encouraging. On the basis of a limited number of analyses of NBS orchard leaves (SRM No. 1571) containing about 2.3 μg/g chromium, relative standard deviations by two different analysts varied from ±5% to ±12% and accuracies (recovery from standard sample) exceeded 95% (Li and Hercules, 1974; Seitz and Hercules, 1973). Recently a centrifugal fast analyzer was used for a rapid chemiluminescence analysis of chromium(III) in water (Bowling et al., 1975).

The chemiluminescence method of analysis is not a mature, established analytical procedure; much more experience is required to define its usefulness and limitations. However, its economy, speed, and extraordinary sensitivity offer promise of usefulness in the analysis of metals at the ultratrace level, especially for chromium in biologic materials.

2.3.3 Comparison of Analytical Methods

Until the last decade or two, the spectrophotometric method utilizing the chromium diphenylcarbazide reaction was the most widely used technique for determining chromium. During the last few years, however, this method has been largely replaced by the more sensitive and convenient atomic absorption spectrometry. Through use of the flame technique, chromium can usually be determined at concentrations equal to or less than that established for drinking water standards without prior concentration. Considerably greater sensitivity can be achieved using the newer flameless variations of atomic absorption spectrometry, with some loss of convenience. In general, the sensitivity, precision, and accuracy attainable by atomic absorption techniques are adequate for most inorganic samples of environmental interest. The usefulness of atomic absorption techniques for analysis of chromium in organic media is not so well defined. The concentration of chromium in many such samples is below the detection level of the flame method unless unusually large samples are used. However, even if large samples are available, the extensive preanalysis processing required by such samples can introduce considerable error. In principle, this dilemma should be resolved by the use of flameless atomic absorption; however, evidence is accumulating that chromium in some biological media behaves differently from inorganic chromium: it may be lost to detection by atomic absorption upon direct placement of the sample in the graphite furnace (Masironi, Wolf, and Mertz, 1973; Maxia et al., 1972; Mertz, 1974; Wolf, Mertz, and Masironi, 1974). The flameless atomic absorption method can still be applied to the determination of chromium in some organic samples such as sugars, however, if the element is converted to the inorganic form by oxygen plasma ashing before introducing the sample into the furnace (Wolf, Mertz, and Masironi, 1974). Conventional techniques for converting chromium in organic samples to the inorganic form should be considered suspect until their validities are rigorously established by the use of appropriate reference standards (Mertz, 1974) (see also Section 2.3.1).

Neutron activation analysis is widely used to determine chromium and other elements in environmental samples; it is probably second only to atomic absorption spectroscopy in frequency of use. This popularity stems from three factors: the great sensitivity of the method, its applicability to a variety of sample types with little or no preanalysis processing, and its ability to determine a variety of elements with the irradiation of a single sample. If many elements must be determined, the cost per element is small by this technique. The use of neutron activation analysis to determine chromium normally requires a cooling period of several weeks if postirradiation separations are not performed. Thus, the technique is not suited for on-line or rapid analyses of chromium. However, if postirradiation separations are made, very precise analyses can be obtained in about a day (McClendon, 1974).

Emission spectroscopy is a well-established analytical method capable of satisfactorily determining many elements simultaneously in a variety of environmental samples. With plasma excitation, the method is adequately sensitive and accurate for most environmental samples. Similar comments apply to spark-source mass spectroscopy with isotope dilution.

The importance of x-ray fluorescence as an analytical method for environmental samples has been greatly expanded by the recent development of the energy-dispersive mode of operation. With this feature, rapid, as well as sensitive, multielement analyses can be performed. This variant of the standard x-ray analysis technique is not yet mature; also, problems relating to sample preparation exist. However, with seasoning, this technique appears very attractive for sensitive multielement analysis of environmental samples.

2.3.3.1 Standardization — Trace-level determinations of chromium are required in an extensive variety of samples: atmospheric particulates and mists, fresh and marine waters, industrial waste effluents, sludges, soils and sediments, and ores and metals as well as plant and animal tissues and fluids. Reliable analyses require standard procedures for the collection, preparation, and storage of these specimen types and standard methods for concentrating or separating the chromium from the various materials. Achievement of this task is only in the initial stages; earliest efforts have been directed toward development of procedures for drinking water, groundwater and surface waters, and domestic and industrial waste effluents. *Standard Methods for the Examination of Water and Wastewater*, 13th ed., 1971, published jointly by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation, prescribes standard sample handling techniques and analytical procedures for many metals and includes spectrophotometric and atomic absorption techniques for chromium at the trace level. More recently, the U.S. Environmental Protection Agency (EPA) published the *Handbook for Analytical Quality Control in Water and Wastewater Laboratories*, 1972, which defines standards useful in many aspects of the work. In a companion volume, *Manual of Methods for Chemical Analysis of Water and Wastes*, 1974, the EPA established standard procedures for determining many constituents of water samples, including the analysis of trace levels of chromium by atomic absorption spectrometry. However, much remains to be done in this area.

One of the most pressing needs is the greater availability of standard materials representative of environmental samples. The National Bureau of Standards (NBS) supplies orchard leaf, tuna meal, bovine liver, and brewer's yeast as standard reference materials for the analysis of biological material. Chromium concentrations in most of these materials are now being certified. The EPA in cooperation with the NBS has made up four environmental standards: fly ash, coal, oil, and gasoline. Concentrations of many of the elements of prime environmental concern in these reference materials are established. Thus far, no standard reference natural water samples are available, but the EPA will supply six concentrated water reference samples which, when diluted as prescribed, will give different concentrations of arsenic, cadmium, chromium, copper, lead, selenium, and zinc in the parts per billion concentration range. These samples are available from J. A. Winter, Methods Performance Evaluation Activity, National Environmental Research Center, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268 (Robertson and Carpenter, 1974).

2.3.3.2 Interlaboratory Comparisons — Relatively few interlaboratory comparisons of chromium analyses at the trace level were reported in the literature. In a study conducted by the Methods Development and Quality Assurance Research Laboratory, Cincinnati, Ohio, six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, iron, manganese, lead, and zinc were added to natural water samples (U.S. Environmental Protection Agency, 1974). Samples were distributed to various laboratories for analysis by atomic absorption spectrometry. The statistical results for chromium are given in Table 2.8. With the exception of one sample, good accuracies were reported by the participating laboratories; however, interlaboratory precision was poor.

The United States Geological Survey (Water Resources Laboratory, Denver, Colorado) conducts a continuing interlaboratory comparison program for water

Table 2.8. Interlaboratory study of chromium analysis by atomic absorption spectrophotometry

Number of labs	True values (μg/liter)	Mean value (μg/liter)	Standard deviation (μg/liter)	Accuracy as percent bias
74	370	353	105	-4.5
76	407	380	128	-6.5
72	74	72	29	-3.1
70	93	84	35	-10.2
47	7.4	10.2	7.8	37.7
47	15.0	16.0	9.0	6.8

Source: U.S. Environmental Protection Agency, 1974, p. 106.

analysis. Chromium results from several of these samples, which cover a period of approximately five years ($\sim$1971 to 1976), are given in Table 2.9. Relative standard deviations show definite improvement during the period, dropping from 70% to 100% in the early rounds to 20% to 30% for the later ones. The total range of reported values remains disturbingly large.

Parr (1974) reported on a study of NBS bovine liver that involved ten laboratories and the range between the high and low result was over 300 (see Section 2.3.1). Pierce et al. (1976) used bovine liver, urine, serum, and wheat in an interlaboratory comparison which also compared results from several methods of analysis. The quality of the results seemed to depend more on the sample matrix than on the analytical method. The range between high and low results for bovine liver was about a factor of four. Chromium in bovine liver is soon to be certified at 90 ± 15 ng/g (Rook and Wolf, 1977).

In a recent study (Von Lehmden, Jungers, and Lee, 1974) by the EPA to monitor trace elements in fuels, nine laboratories using similar analytical methods were asked to determine the concentration of 28 elements, including chromium, in the same fuel and fly-ash matrices. The analytic methods included neutron activation analysis, atomic absorption spectrometry, spark-source mass spectrometry, optical emission spectrometry, anodic stripping voltammetry, and x-ray fluorescence. The reported values of chromium in coal ranged from 3.4 to $\sim$30 ppm; in fly ash, from 80 to 500 ppm; in residual fuel oil, from 0.7 to 4 ppm; and in gasoline, from <0.001 to <0.3 ppm.

There appears to have been significant improvement in the ability to measure chromium during the past five years but the ranges reported are

Table 2.9. Interlaboratory comparison results from water analysis of chromium

SRW number	Total range (μg/liter)	Mean ± standard deviation (outliers rejected)	Relative standard deviation
28		19.2 ± 14.3	74
32		11 ± 11	100
38	0-90	45 ± 24	33
39	0-40	7.9 ± 6.3	80
44	4-50	8.2 ± 2.8	34
45	7-70	18.9 ± 6.2	32
48	15-45	31.8 ± 7.0	22
49	10-32	16.5 ± 5.9	36
52	3-40	6.3 ± 2.3	36
53	10-90	20.0 ± 5.0	25
56	10-110	39.4 ± 11.9	30
57	0-25	9.5 ± 1.7	18
59	14-43	30.2 ± 6.5	21

Source: U.S. Geological Survey Water Resources Laboratory, Denver, Colo.

still disturbingly large. The ranges illustrate the difficulties in measuring traces of chromium and emphasize anew the importance of certified reference materials such as those now being provided by the National Bureau of Standards.

SECTION 2

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SECTION 3

BIOLOGICAL ASPECTS IN MICROORGANISMS

3.1 SUMMARY

The limited data on the metabolism and toxicity of chromium show that most microbes are able to absorb some chromium. Internal chromium concentrations for microbes vary, but many samples have about 1 ppm chromium, a value similar to that found in many plants. Chromium has not been shown to be an essential element for any group of microorganisms. Toxicity for many microbes occurs at chromium concentrations of 0.05 to 5 ppm, although exact tolerances depend on the particular species. Chromium inhibits a variety of metabolic processes such as nitrogen fixation, photosynthesis, and protein synthesis; no data defining mechanisms of toxicity were found. Comparative data indicate that chromium(VI) is more toxic than chromium(III).

3.2 METABOLISM

The metabolism of chromium in microbes has scarcely been studied. Although isolated reports have given evidence that chromium addition stimulated growth (Pratt and Dufrenoy, 1947) or certain metabolic systems (Horecker, Stotz, and Hogness, 1939), most reports have shown growth inhibition at moderate chromium concentrations. No studies have conclusively demonstrated that chromium is an essential element in microbes.

3.2.1 Uptake

Little information was found on the mechanisms or kinetics of chromium uptake by microbes. Roberts and Marzluf (1971) demonstrated that chromate was actively taken up by the sulfate transport system in *Neurospora crassa*. A similar mode of transport apparently exists in the bacterium *Salmonella typhimurium* (Ohta, Galsworthy, and Pardee, 1971; Pardee et al., 1966) and in the fungus *Aspergillus nidulans* (Arst, 1968). In fact, a common method for selecting microbial mutants deficient in sulfate uptake is by selection for chromate resistance (Ohta, Galsworthy, and Pardee, 1971). Resistance is assayed by the ability to grow in the presence of 26 ppm chromium(VI) (0.5 m*M* Na_2CrO_4) (Pardee et al., 1966).

Radiochromate (picocuries per gram wet wt) was measured in plankton from the Columbia River (Watson et al., 1969). Chromium is released into the river by the Hanford Reactor. Uptake by these plankton was assumed to occur by adsorption rather than by assimilation. However, no experimental evidence was given to support this contention. The chemical form of chromium in natural waters must also be considered in the assessment of adsorption and assimilation phenomena.

Experiments with ^{51}Cr have shown that the alga *Navicula* sp. and a bacterium (species not specified) sorbed chromium (ca. 40% to 50% of ^{51}Cr taken up in 24 hr) under those particular experimental conditions (Calow and Fletcher, 1972). The data did not distinguish between adsorption and absorption. The amount of ^{51}Cr lost from *Navicula* and bacteria over a 48-hr period was less than 4% of ^{51}Cr absorbed.

An interesting relation between chromium (as trivalent chromium) uptake and glucose concentration occurs in brewer's yeast. Whereas uptake of trivalent ^{51}Cr did not occur in Sabouraud medium in either log or stationary phase cells, addition of glucose increased chromium uptake 2000% after 13 days. Uptake of manganese or iron was not increased. Uptake was independent of the trivalent chromium concentration (0.0001 to 1 ppm); these concentrations did not stimulate growth (Burkeholder and Mertz, as cited in Mertz, 1969).

3.2.2 Concentration

Information on chromium concentration in microbes is rather sparse, but existing data illustrate that a rather broad concentration range can be found and that the internal concentration is probably related to the concentration in the external medium (Table 3.1).

Chromium concentrations for a variety of plants, including algae and fungi, are listed in Table 4.15. The concentrations ranged from 0.65 to 27 ppm chromium and are similar to concentrations found in higher plants. Table 3.2 gives chromium concentrations in some multicellular marine algae; the observed range is from about 0.4 to 12 ppm chromium with a typical concentration of about 1 ppm. No data on the relationship between chromium concentrations in water and in the plants were found. Fukai and Brokey (1965) suggested that surface contamination of water plants may account for part of the observed chromium content. Boothe and Knauer (1972) reported that the brown algae *Macrocystis pyrifera* contained 5.0 ± 3.5 ppm chromium on an ash weight basis.

Data such as these must be used with caution, however, because of the analytical uncertainties discussed in the previous chapter. Relative chromium values from a given laboratory are probably trustworthy but absolute values and comparative values between laboratories must be regarded as very uncertain. This situation will remain, especially for older data, until the reasons for the large analytical errors are explained.

3.2.3 Biotransformation and Elimination

No information was found on the metabolism of chromium within the cell when supplied as either trivalent or hexavalent chromium or on the possible elimination of chromium from living cells.

3.3 EFFECTS

The major effect reported for chromium is growth inhibition of a variety of organisms. However, in most cases, studies were not designed to determine the maximum concentrations tolerated without metabolic impairment.

Table 3.1. Microbial concentration of chromium

Organism	Chromium concentration (ppm dry wt)	Sample area	Reference
Sphaerotilus sp. (bacterium)	284	Japanese river, below pollution effluent outfall	Loutit, Patrick, and Malthus, 1973
Zooplankton	6-12	Control region of N.Y. Bight	Vaccaro et al., 1972
	7-11	Acid-iron waste disposal area, N.Y. Bight	Vaccaro et al., 1972
	8-137	Monterey Bay, Calif.	Martin and Knauer, 1973
Microplankton	0.6-3.7	Monterey Bay, Calif.	Martin and Knauer, 1973
Phytoplankton	1.3-21.4	Pacific Ocean	Martin and Knauer, 1973
Plankton	3.5		Schroeder, Balassa, and Tipton, 1962
Fungi	1.5		Schroeder, Balassa, and Tipton, 1962
Coral			Livingston and Thompson, 1971
Solenosmilia	<2	Jamaican deep-ocean region	
Desmophyllum	1-1.2	Jamaican deep-ocean region	
Caryophyllia	<2-3	Jamaican deep-ocean region	
Trochocyathus	1.5	Jamaican deep-ocean region	
Dendrophyllia	2	Jamaican shallow-ocean region	
Madracis	4	Jamaican shallow-ocean region	
Cladocora	2	Jamaican shallow-ocean region	
Anomocora	2	Jamaican shallow-ocean region	
Bathycyathus	4	Jamaican shallow-ocean region	
Unidentified	33		
Lichens		Collected from sandstones	LeRoy and Koksoy, 1962
Umbilicaria hyperborea	100-150		
Parmelia conspersa	50		
Lecanora rubina	30		
Caloplaca elegans	150		

Table 3.2. Chromium content of algae

Species	Place and date of collection	Chromium content (ppm)
Enteromorpha linza (green algae)	Toulon (M)[a] Aug. 1963	1.6
Enteromorpha ralfsii (green algae)	Cap Breton (A)[b] Jan. 1964	0.9
Enteromorpha sp. (green algae)	St.-Raphaël (M) July 1964	0.4
Ulva lactuca (green algae)	Arcachon (A) Jan. 1964	1.4
	St.-Raphaël (M) July 1964	0.4
Codium elongatum (green algae)	Monaco (M) Sept. 1963	0.4
Cystoseira myriophylloides (brown algae)	Toulon (M) Aug. 1963	1.4
Cystoseira fimbriata (brown algae)	St.-Raphaël (M) July 1964	1.0
Fucus ceranoides (brown algae)	Bayonne (A) Jan. 1964	0.6
Fucus vesiculosus (brown algae)	Cap Breton (A) Jan. 1964	1.0
	Arcachon (A) Jan. 1964	0.6
Jania rubens (red algae)	Toulon (M) Aug. 1963	4.1
Lithophyllum incrustans (red-calcarious algae)	Cap Martin (M) June 1962	12.1

[a] M = Mediterranean coastal waters.
[b] A = French Atlantic littoral.

Source: Adapted from Fukai and Broquet, 1965, Table 1, p. 4. Reprinted by permission of the publisher.

3.3.1 Algae

Growth inhibition data reported by Hervey (1949) for seven algal species demonstrated that certain species were more tolerant of chromium (added as $K_2Cr_2O_7$) than others (Table 3.3). Additionally, small amounts of chromium stimulated growth (Table 3.4). Optimal growth, however, in five of the seven species was at chromium concentrations of <0.32 ppm.

Wium-Andersen (1974) found a decrease in growth over a four-day period in the algal species *Nitzschia palea* (diatom) and *Chlorella pyrenoidosa* at

Table 3.3. Approximate concentration ranges of chromium which completely inhibited growth in seven species of algae (ppm)

Organism	H-2 growth medium			H-2 modified growth medium		
	15 days	33 days	56 days	15 days	33 days	56 days
Chorella variegatus	1.6-3.2	1.6-3.2	6.4-16.0	1.6-3.2	3.2-6.4	6.4-16.0
Chlorococcum humicola	1.6-3.2	3.2-6.4	3.2-6.4	3.2-6.4	3.2-6.4	3.2-6.4
Scenedesmus obliquus	3.2-6.4	3.2-6.4	3.2-6.4	1.6-3.2	1.6-3.2	1.6-3.2
Lepocinclis steinii	0.032-0.32	0.32-1.6	0.32-1.6	0.032-0.32	0.32-1.6	0.32-1.6
Flagellate #46	0.032-0.32	0.32-1.6	0.32-1.6	0.32-0.32	0.32-1.6	1.6-3.2
Diatom #26	No growth[a]	0.032-0.32	0.32-1.6	0.32-1.6	0.32-1.6	0.32-1.6
Diatom #47	No growth[a]	0.032-0.32	0.032-0.32	0.032-0.32	0.032-0.32	0.32-1.6

[a] The lag period for both these organisms was so extended in H-2 medium that even the controls showed no growth in 15 days.

Source: Adapted from Hervey, 1949, Table 2, p. 6. Reprinted by permission of the publisher.

Table 3.4. Greatest concentration of chromium which permitted growth equal to or better than controls (no chromium) in seven algal species (ppm)

Organism	H-2 growth medium			H-2 modified growth medium		
	15 days	33 days	56 days	15 days	33 days	56 days
Chorella variegatus	0.0001	0.32	1.6	0.00032	0.32	3.2
Chlorococcum humicola	0.32	0.32	0.32	0.0	0.32	0.32
Scenedesmus obliquus	0.32	0.32	0.32	0.0	0.32	0.32
Lepocinclis steinii	0.032	0.032	0.32	0.032	0.032	0.32
Flagellate #46	0.032	0.032	0.32	0.0	0.032	0.32
Diatom #26	[a]	0.32	0.32	0.032	0.32	0.32
Diatom #47	[a]	0.032	0.032	0.032	0.032	0.32

[a] No growth in any tubes, including controls.

Source: Adapted from Hervey, 1949, Table 2, p. 6. Reprinted by permission of the publisher.

$Cr_2O_7^{2-}$ concentrations of 50, 150, and 300 ppb (Figure 3.1). No growth stimulation was observed at any of the concentrations used; increased iron concentration (24 ppb) did not counteract the toxicity. In this study, photosynthesis in *Nitzschia* was inhibited 25% at a $Cr_2O_7^{2-}$ concentration of about 350 ppb and 50% at a concentration of about 750 ppb. In *Chlorella*, about ten times more chromium was necessary to inhibit photosynthesis by the same degree as in *Nitzschia*. Since chromium had no inhibitory effect at low light intensities (where light would be the limiting factor), the authors concluded that chromium inhibition occurred in the dark processes of photosynthesis. More information is needed, however, on the mechanism of growth inhibition because the kinetics of inhibition of growth and photosynthesis are not similar.

Chromium concentrations between 0.01 and 0.50 ppm did not stimulate growth in *Chlorella* cultures. Growth inhibition occurred at concentrations greater than 0.50 ppm (Nollendorf, Pakalne, and Upitis, 1972). Toxicity of chromium could be decreased by increasing the concentrations of other trace elements, by adding ethylenediaminetetraacetic acid (EDTA) to the medium, or by increasing the iron concentration. Chromium adsorption increased at toxic chromium levels. A 50% reduction in cell number occurred in *Nitzschia linearis* W. Sm. after 120 hr of culture with 0.21 ppm trivalent chromium (Patrick, Cairns, and Scheier, 1968).

Upitis, Pakalne, and Nollendorf (1973) found 102%, 86%, 71%, 62%, and 36% of control biomass of *Chlorella* sp. grown in culture with 0.1, 1, 2, 3, and 5 ppm chromium, respectively (form of chromium not specified). Although several trace elements essential to growth were tested, only iron (10 and 45 ppm) eliminated the growth inhibition of 2 ppm chromium in the culture solution. Similar phenomena of amelioration by addition of trace elements were shown for growth inhibition by cadmium and nickel. The existence of specific antagonistic ions which decrease chromium ion toxicity is well documented in certain cases (Epstein, 1972).

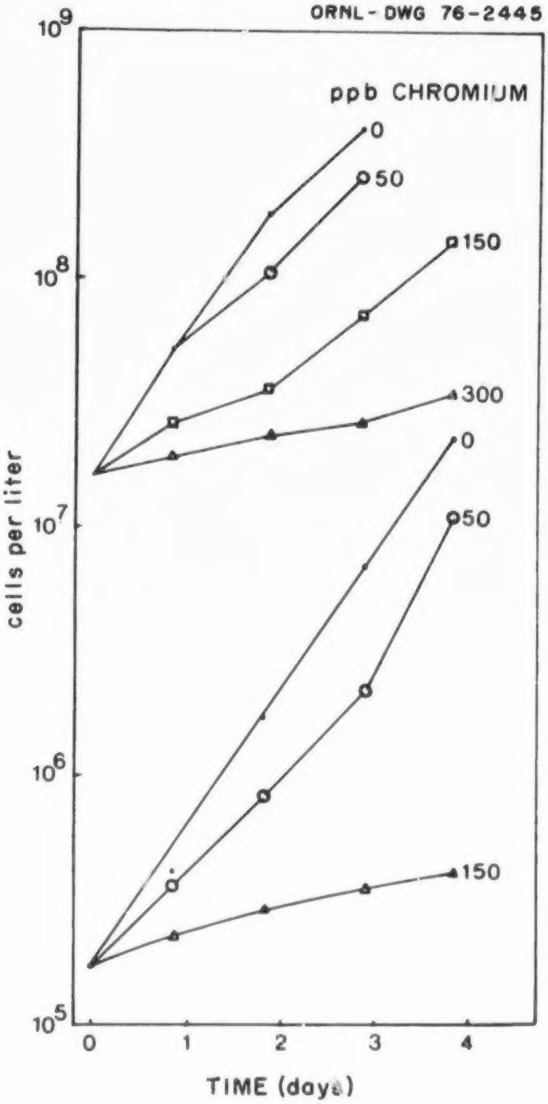

Figure 3.1. The effect of different concentrations of chromium on the growth of *N. palea*. Source: Adapted from Wium-Andersen, 1974, Figure 1, p. 309. Reprinted by permission of the publisher.

Garton (1973) grew the alga *Selenastrum capricornutum* in culture with chromate concentrations ranging from 0.0139 to 13.9 ppm (Figure 3.2) and observed almost complete inhibition of growth at concentrations greater than 1.39 ppm chromium. The object of the study was to identify toxic components found in cooling-tower blowdown. Concentrations of CrO_4^{2-} within the range used in this study are found in cooling-tower blowdown; thus, a potential environmental hazard exists. As indicated by the author, toxicity data are needed not only for individual compounds found in the blowdown but also for various combinations of these compounds. The concentrations

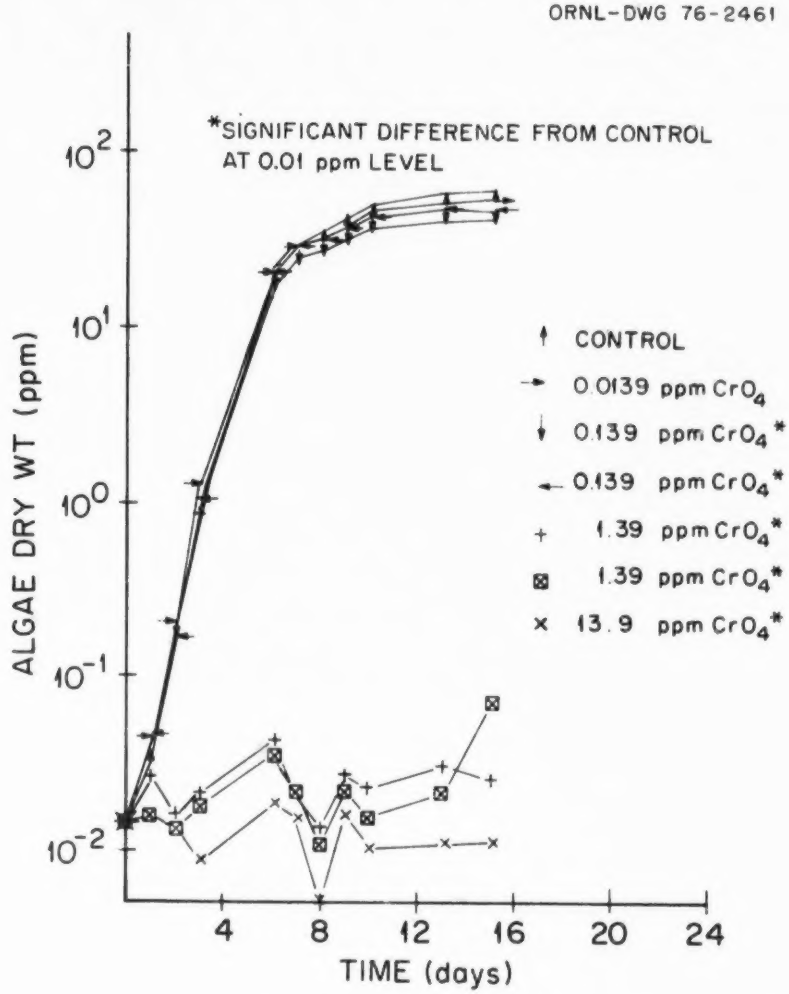

Figure 3.2. Inhibitory effects of sodium chromate concentrations on the alga *Selenastrum capricornutum*. Source: Adapted from Garton, 1973, Figure 2, p. 291. Reprinted by permission of the publisher.

of $Cr_2O_7^{2-}$ which inhibited growth of the algae *Scenedesmus*, *Navicula seminulum*, and *Macrocystis pyrifera* were 0.7, 0.2, and 1.0 ppm, respectively (North, Stephens, and North, 1973).

Pollutants may have a differential effect on members of a mixed population. In studies aimed at delineating the role of trace elements in the management of nuisance growths in aquatic systems, Patrick, Boot, and Larson (1975) studied the effects of several trace elements, including chromium, on algal community structures. Experiments were conducted during different months of the year to determine whether changes in natural conditions influenced the effects of the trace elements. Mixed filamentous and diatom algal populations were suspended in test chambers in stream waters. While other characteristics were held constant, various concentrations of the trace element compounds were added to the water. At a chromium concentration (potassium dichromate) of 40 to 50 ppb, diatoms remained dominant and diversity was high. At average concentrations of 95 to 97 ppb, the diatom diversity was reduced although the diatoms remained dominant; at average concentrations of 397 ppb, diatoms were completely replaced by blue-green algae and the green alga *Stigeoclonium lubricum*. Differences in biomass and in uptake of chromium occurred during the year. For instance, at 50 ppb chromium in the water the accumulation was 1450 ppm (micrograms chromium per gram of dried biomass) in March to April, whereas in May it was only 500 ppm. However, biomass was higher in May and dilution was therefore a more important factor. At 100 ppb chromium results were similar, while at 400 ppb the difference was accentuated — an accumulation of 3350 ppb in March to April and only 900 ppb in May. In the period July to August, accumulation at the 400-ppb level was 2000 ppm. In general, there was a good correlation between the amount of accumulation of chromium per gram of biomass, the ^{14}C uptake, and the development of a blue-green algal flora.

Because blue-green and green algae are less subject to predator pressure (mostly aquatic insect larvae) than are diatoms, their growth should be restrained. These studies indicate the need for regulation of trace element levels so that diversity, productivity, and openness of waterways can be maintained.

3.3.2 Protozoa

Concentrations of chromium(VI) (supplied as $K_2Cr_2O_7$) which were "lethal" to various protozoa varied from 160 ppm for *Peranema* to 5000 ppm for *Paramecium caudatum*, while "tolerated" concentrations ranged from 718 ppm for *Chilomonas* to 1000 ppm for *P. caudatum* (Ruthven and Cairns, 1973). "Lethal" concentration was defined as the lowest concentration at which all organisms died within 10 min of exposure, and "tolerated" concentration was the highest concentration at which "some" organisms remained alive after 3 hr. These data are of limited value because of the high concentration of chromium used and because of unsuitable viability criteria.

Chromate concentrations from 10 to 100 μM accelerated growth of promastigotes of *Leishmania tarentolae*, a protozoan blood parasite, cultured in medium with [^{35}S]taurine as the sole sulfur source (Sheets and Krassner, 1974). Chromate also enhanced incorporation of ^{35}S label from taurine into cell fractions. Increased growth with chromate did not occur, however, when inorganic sulfate was the sole sulfur source. Presumably, the chromium effect is related to sulfur metabolism in the promastigotes.

3.3.3 Fungi

Mertz (1969) has reviewed the sparse literature on the effects of chromium on yeast. Chromates in broad range of concentrations (6 to 800 ppm) can stimulate yeast fermentation, although similar stimulation can be caused by other agents (acidity, heat, salts, and hypotonic solutions). Toxicity of trivalent chromium to brewer's yeast was reported at concentrations of 200 ppm chromium.

In studies to determine how the incorporated metal influenced yeast metabolism, Burkeholder and Mertz (1966) added 0.1 ppm trivalent chromium to cultures and observed increased CO_2 production (after a 3-hr lag) as compared with unsupplemented controls. Addition of glucose tolerance factor, a chromium complex required for normal glucose utilization (Section 6.3.1.1), or yeast cell fractions containing chromium produced an immediate stimulation of CO_2 production. Thus, chromium is important for biological activity, although the exact mechanism of its role in metabolism is undefined.

Sulfuric acid—dichromate mixtures have long been used to clean glassware. Even exhaustive rinsing of the glassware does not remove all the $Cr_2O_7^{2-}$ ions that are sorbed onto the glass surface and the amount remaining can inhibit some enzymes and the growth of certain microbes. Richards (1936) found that as little as 0.1 ppb $Cr_2O_7^{2-}$ inhibited growth of yeast and "other microbes."

Few studies were found on chromium effects on fungi other than yeast. The median effective dose of trivalent chromium [as $Cr(NO_3)_3$] which inhibited germination of the fungi *Alternaria tenuis* and *Botrytis fabac* was 4.5×10^{-6} and 12.5×10^{-6} *M*, respectively (Somers, 1961). Natural infections of corn kernels with *Aspergillus flavus* were associated with increased levels of trace elements in the kernel (Lillehoj, Garcia, and Lambrow, 1974). Addition of 5 to 10 μg of chromium, manganese, cobalt, or cadmium per gram of germ to a growth medium of defatted corn germ increased aflatoxin production by *Aspergillus*. Since phytate (inositol hexaphosphate) present in corn germ strongly binds trace elements, these elements might not be biologically available for microbial growth. Results of Lillehoj, Garcia, and Lambrow (1974) suggested that aflatoxin production may be a method of measuring availability of trace elements to the fungus. Ashida (1965), who reviewed fungal adaptation to metal toxicants, cited only one case of acquired resistance to chromium, and that case occurred in yeast.

With any organism the possibility exists of finding a strain with increased tolerance or sensitivity to the chemical under study. For instance, although the type of resistance involved is not clear, strains of the brown rot fungus (*Poria vaillantii*) which demonstrate increased resistance to a copper-chrome-arsenate wood preservative have been isolated (Da Costa, 1959). However, the resistance may be due to increased resistance to arsenic. The diversity, density, and succession of microbial invaders on exposed woods have been studied by a number of workers (Greaves, 1972); the results suggest that some microbes have a certain tolerance to these preservatives.

3.3.4 Bacteria

Little information was found for effects of chromium on bacteria. In *Bacillus megatherium*, LD_{50} values were 144 ppm chromium(III) and 76 ppm chromium(VI) (Ludvick, as cited in Eye, 1974). Growth of *Staphylococcus aureus* in a dilute synthetic medium was inhibited by the addition of 1 ppm $Cr_2O_7^{2-}$. Growth inhibition in a beef extract—peptone broth medium required a concentration of almost ten times as much, presumably because protection was conferred by the macromolecular constituents of the broth (Henry and

Smith, 1946). Nitrogen fixation in *Azotobacter chroococcum* was stimulated by 10^{-5} to 10^{-4} g/liter of K_2CrO_4 and was inhibited by 10^{-3} g/liter of K_2CrC_4 (Egorova and Shohegiov, 1970). In higher concentrations, K_2CrO_4 inhibited growth of these bacteria.

Weinberg (1964) found that "subbactericidal" concentrations of various trace elements (chromium, molybdenum, tungsten, selenium, and tellurium) supplied before or within 2 hr after manganese addition suppressed sporulation in *Bacillus*. Manganese, in concentrations larger than that required for vegetative growth, was necessary for sporulation. Chromium (60×10^{-6} *M*) added 3 hr after manganese addition actually increased the sporulation.

Increased sensitivity to chromium has been observed in a mutant of *Salmonella typhimurium* (Corwin et al., 1966). The authors first observed that ethylenediaminetetraacetic acid (EDTA) in the solid growth medium allowed growth of tryptophan-deletion mutants and found that their agar contained chromium. Experiments showed that the chromium concentration in the agar was sufficient to inhibit growth of the mutant but not growth of the normal type. Differences in toxicity susceptibility to other trace elements could not be demonstrated between mutant and normal type. At 500 μ*M* $CrCl_3$, normal strains showed little decrease in growth, whereas $CrCl_3$ at concentrations as low as 10 to 20 μ*M* caused complete growth inhibition in the mutants. The nature of the mutation is unknown; trivalent chromium concentrations within the normal and mutant strains were not determined.

Two *Escherichia coli tonB-trp* deletion mutants which are sensitive to chromium(III) and require high iron concentrations for optimal growth were described by Wang and Newton (1969*a*). The chromium sensitivity can be reversed with high iron concentrations. These data, along with other lines of evidence, suggest that the deleted genetic information is responsible for active iron transport and that "residual iron transport" is inhibited by the chromium(III) ion.

A point mutant of *E. coli* which is sensitive to trivalent chromium and requires a high concentration of iron for growth had the active iron uptake system but could not synthesize a natural chelator, 2,3-dihydroxybenzoylserine (DHBS), specific for iron (Wang and Newton, 1969*b*). The mechanism by which chromium(III) inhibits residual iron uptake is not known, but it may involve competition with iron(III) for entry.

There is evidence that hexavalent chromium compounds are mutagenic. Tryptophan revertants in the *E. coli* mutation assay system were produced by Na_2CrO_4, K_2CrO_4, and $CaCrO_4$ (0.05 to 0.20 micromole per culture plate). No revertants were found using the soluble compound $Cr_2SO_4K_2SO_4 \cdot 2H_2O$ or with soluble salts of tungsten or molybdenum (neighboring class VI-B elements), which indicated specificity. Only hexavalent chromium was mutagenic in this system (Venitt and Levy, 1974). These authors suggested that chromium specifically attacks GC base pairs within the DNA molecule, giving GC-AT transitions.

SECTION 3

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SECTION 4

BIOLOGICAL ASPECTS IN PLANTS

4.1 SUMMARY

Chromium is present in all soil types (Section 7) and in plants growing on these soils, but it has not been shown to be an essential element for plants. Plants take up chromium through either root or leaf surfaces, but little chromium is translocated from the site of adsorption unless it is supplied in chelated form. Natural chelates of chromium within the soil probably occur, but they have not been studied.

Chromium concentrations in plants growing on normal soils range from about 0.1 to 5 ppm, with most values less than 1 ppm. Plants growing on serpentine soils show a much wider concentration range, from 1 ppm to 3000 ppm chromium in ash. Subterranean plant parts have higher chromium concentrations than do aerial parts.

Plants growing near cooling towers contain elevated levels of chromium. Concentrations of chromium in plants growing near smelters have not been reported. Wastes from chromate-producing smelters are very toxic to vegetation necessitating revegetation techniques for reclamation of contaminated areas.

Serpentine soils contain high levels of chromium which contribute to the low fertility of these soils. The major factors are probably low absolute calcium levels, low calcium to manganese ratios, low trace element levels, or nickel toxicity. The cause of infertility may vary with the specific serpentine soil under examination.

High chromium concentrations caused chlorosis in beans and oats and stunting in tobacco, an especially sensitive plant, and maize. There is a lack of experimental work on the effects of the different chemical forms of chromium on plants. From limited data, hexavalent chromium appears to be more toxic than trivalent chromium; both forms affect plants at relatively low concentrations (about 1 to 10 ppm).

4.2 METABOLISM

The metabolism of chromium in plants includes uptake, translocation, concentration and distribution, and elimination. Chromium can undergo few chemical changes within the cell other than oxidation-reduction. Although complex formation could occur within the cell (Section 4.2.3), few studies on subcellular distribution or interactions of chromium in plant systems have been reported.

4.2.1 Question of Essentiality

The question of whether chromium is an essential element for plants has not been answered. Some authors reported that the addition of chromium compounds to soil resulted in increased yield. In reviewing these reports, Pratt (1966) concluded, "These stimulative effects have been small and others have been erratic; most have remained unverified." A review by Mertz (1969) cited reports of increased crop yields in Germany, France, Poland, and Russia as a result of chromium application to soils. Mertz concluded that small amounts of chromium are beneficial for plant growth, but he noted the complexity of assessing chromium availability in soils and of determining how chromium stimulates yield. Additional support for this view comes from increased yields of wheat, rye, oats, corn, and peas grown in a sand and water culture containing trivalent chromium (Scharrer and Schropp, 1935, cited in Mertz, 1969).

Huffman and Allaway (1973*b*), however, demonstrated that romaine lettuce, wheat, and beans grew normally in culture solution experiments with purified salts. Final chromium concentration was 3.8×10^{-4} micromole. Thus, if chromium is required by these plants, it is required at concentrations less than 3.8×10^{-4} micromole.

Improved plant response after addition of the element to soil is not conclusive evidence for essentiality. Arnon and Stout (1939) stated,

> An element is not considered essential unless (a) a deficiency of it makes it impossible for the plant to complete the vegetative or reproductive stage of its life cycle; (b) such deficiency is specific to the element in question, and can be prevented or corrected only by supplying this element; and (c) the element is directly involved in the nutrition of the plant quite apart from its possible effects in correcting some unfavorable microbiological or chemical condition of the soil or other culture medium. From that standpoint a favorable response from adding a given element to the culture medium does not constitute conclusive evidence of its indispensability in plant nutrition.

Thus, while chromium is an essential element for humans (Section 6.3.2), no conclusive evidence exists for its essentiality in plants.

4.2.2 Uptake

Plants take up many substances by absorption through either root or leaf surfaces. Absorption of most minerals typically occurs through root uptake, but it can also occur through aboveground surfaces exposed to materials in the air. Several factors affect chromium absorption by plants and the availability of chromium in the soil: physical and chemical properties of the chromium compounds, pH effects on reactivity and solubility phenomena, presence of organic chelating compounds within the soil, interactions with other soil minerals, and the ability of the given species to absorb chromium under a range of environmental factors such as carbon dioxide and oxygen concentrations (Black, 1968).

The mechanism of chromium uptake is speculative; it may involve the absorption of soluble ions from the soil solution, from adsorbed ions in soil by contact exchange, and from soluble organic-chelated forms (Black, 1968). The specific methods of chromium absorption from the soil are unknown.

The kinetics of absorption of chromium(III)-ethylenediaminetetraacetic acid (EDTA), chromium(III) [as $Cr(NO_3)_3$], and chromium(VI) (as K_2CrO_4) from nutrient solutions were studied in rice (Verfaillie, 1974). Chromium supplied in chelated form entered roots more slowly than either chromium(III) or chromium(VI); the chelated form, however, was transported throughout the plant. Chromium(III) and CrO_4^{2-} were absorbed more quickly (Table 4.1), although less than 2% was transported to aerial parts (Table 4.2). Chromium(III)-EDTA was continuously taken up over the five-day period; stems attained the greatest chromium concentration (Figure 4.1). Chromium(III) has a strong tendency to form chelates and these probably occur in soils, but no data are available to indicate a role in chromium uptake in field situations. The kinetics of chromium(III) uptake were divided into three phases: (1) a rapid phase of adsorption onto root surfaces, (2) absorption [second order kinetics between chromium(III) and an existing pool of biochemical compounds], and (3) a prolonged phase (<10 hr) of metabolic uptake involving delivery to shoots. The kinetics of chromium(VI) uptake showed two stages or mechanisms which could be fitted into the Michaelis equation. Although he had no direct evidence, Verfaillie concluded from kinetic data that chromate was reduced to the chromic state [chromium(III)] by organic matter on the root prior to physiological uptake.

Table 4.1. The rate of chromium absorption by intact rice plants as a function of the chromium concentration in nutrient solution

Concentration level (M)	Cr(III)-EDTA uptake (nmole hr^{-1} gFR^{-1})[a]	K_2CrO_4 intake (nmole hr^{-1} gFR^{-1})	$Cr(NO_3)_3$ uptake phase (nmole hr^{-1} gFR^{-1})
10^{-7}		0.39	0.012
2×10^{-7}		0.58	0.020
5×10^{-7}		0.97	0.047
10^{-6}		1.44	0.088
2×10^{-6}	0.031	1.87	0.13
5×10^{-6}		4.06	0.28
10^{-5}	0.13	6.70	0.35
2×10^{-5}		12.1	0.77
3×10^{-5}			1.70
5×10^{-5}		21.1	2.39
7×10^{-5}			2.92
10^{-4}	0.29	24.9	3.14
Saturation	$V_{max} = 0.35$[b]	$V_{max} = 34.2$	$V_{max} = 4.0$

[a] $nmole^{-1}$ hr^{-1} gFR^{-1} = nanomoles per hour per gram of fresh weight of root.

[b] V_{max} = maximum uptake rate.

Source: Adapted from Verfaillie, 1974, Table I, p. 321. Reprinted by permission of the publisher.

Table 4.2. Distribution pattern of chromium after absorption by intact rice plants

Plant tissue	Percent of total chromium in each plant part		
	Cr(III)-EDTA	K_2CrO_4	$Cr(NO_3)_3$
Roots	9.4	95.7	95.3
Collars	38.8	2.8	2.9
Stems	33.2	0.7	0.9
Leaves	18.6	0.8	0.9
Total	100.0	100.0	100.0

Source: Adapted from Verfaillie, 1974, Table II, p. 322. Reprinted by permission of the publisher.

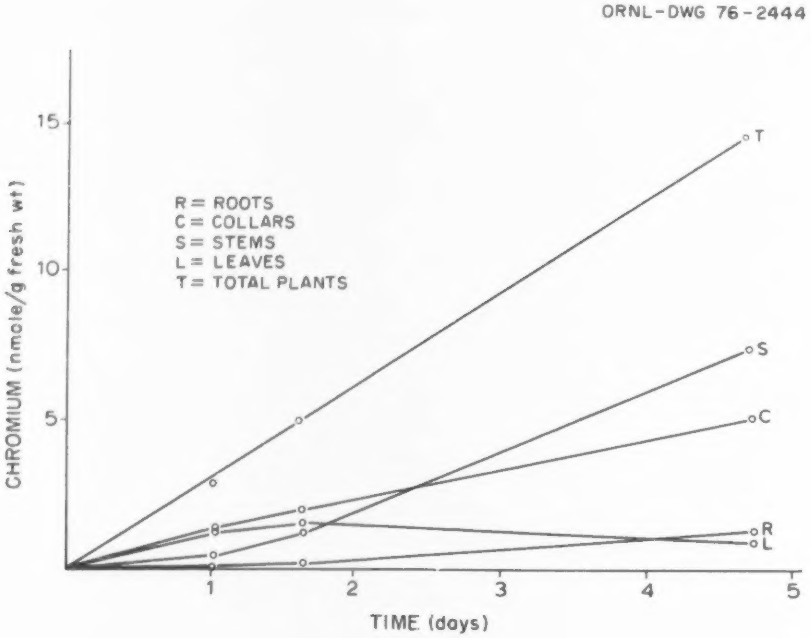

Figure 4.1. The translocation of chromium(III)-EDTA in rice plants. Source: Adapted from Verfaillie, 1974, Figure 13, p. 328. Reprinted by permission of the publisher.

In sand culture experiments, the uptake of CrO_4^{2-} into tobacco leaves, tobacco roots, and corn leaves increased with increasing chromium concentrations in the external medium (Soane and Saunder, 1959). The chromium concentration in corn leaves increased from 4 to 8 ppm when the external chromium concentration was increased from 0 to 10 ppm. Amounts of chromium in tobacco leaves increased from 4 to 34 ppm when the plants were cultured in concentrations of 0 to 10 ppm chromium; over the same range of external concentrations, the chromium content of tobacco roots increased from 13 to 410 ppm. Tobacco was extremely sensitive to chromium; abnormal development occurred at 1 ppm chromium in the culture medium (175 ppm chromium in roots).

Eckert and Blincoe (1970) evaluated the uptake of 14 gamma-emitting isotopes, including ^{51}Cr, from range soil by various forage and weed species. The uptake of chromium was rated as very good in the upper soil horizons for several range species. Decreased uptake was noted for chromium in the lower soil horizons; this was attributed to the decreased solubility of chromium with increasing pH.

Corn grown on soil amended with sludge to give total soil chromium concentrations of 3 to 1360 ppm contained only 1.2 to 2.3 ppm chromium in the tops (Table 4.3) (Mortvedt and Giordano, 1975*b*). Incubation of sludge-amended soils for 21 and 36 weeks prior to planting of corn in the pots did not greatly affect final chromium concentration in the tops. Addition of $Na_2Cr_2O_7$ to soil to give 1, 5, 20, 80, and 320 ppm chromium increased chromium concentrations in corn from the control level (1.5 ppm) to 5.0 and 16.1 ppm at the two highest soil values. Repetition of the above experiment at soil pH 5.5 and 7.0 gave similar results; large increases of chromium in the tissue occurred only at 320 ppm soil chromium.

Again, a note of caution must be added concerning uncertainties in older analytical procedures. Comparisons based on data sets generated in different laboratories, or in one laboratory at different times, may be subject to large errors. Since the data given here are the best available, however, they must suffice for at least tentative comparisons.

The ability of the living cell to take up chromium has led to its use in estimating viability in a cell population (Kumanishi and Yamamoto, 1968). Bourque, Vittorio, and Weinberger (1967) found that increased hexavalent ^{51}Cr incorporation (supplied as CrO_4^{2-}) into sectioned wheat root tips accompanied the increased metabolic state which occurred during vernalization. However, they found little radioactivity in roots incubated with ascorbic acid (to reduce hexavalent to trivalent chromium) prior to incubation with ^{51}Cr-labeled CrO_4^{2-} and thus concluded that only hexavalent chromium could penetrate cells. These data disagree with the results of other experiments (Section 4.2.3) and may possibly be explained by the extensive washing of the root sections in this study. No data were given for chromate added at the same time as the ascorbate.

The chemical form of chromium in a given soil depends on the origin of the chromium compounds. Native chromite, a major form of chromium in the lithosphere, is a mixture of oxides of magnesium, calcium, chromium, iron, and aluminum and is essentially insoluble. Anthropogenic sources could

Table 4.3. Yield and chromium content of corn grown in greenhouse pot experiments in soils with various amendments[a]

Treatment	Rate of chromium application (ppm)	Yield (g/pot)			Chromium in tissue (ppm)		
		Crop 1	Crop 2	Crop 3	Crop 1	Crop 2	Crop 3
Control	0	31	48	30	1.3	2.1	2.0
Sludge A	68	33	50	34	1.2	1.7	2.3
	340	35	45	32	1.2	3.0	5.4
	1360	30	50	31	1.4	1.5	2.0
Sludge B	3	32	49	27	2.3	2.3	3.0
	13	34	48	34	1.4	3.5	1.3
	50	19	51	36	1.4	1.4	0.6
Compost	3	34	51	31	1.1	1.9	2.8
	13	36	47	41	1.1	1.6	1.8
	50	37	46	40	2.0	1.2	0.7
Control (uncontrolled pH)	0	31	48		1.3	2.1	
$Na_2Cr_2O_7$ (uncontrolled pH)	1	32	49		1.5	1.4	
	5	32	50		1.5	1.9	
	20	27	50		2.3	1.9	
	80	4	55		5.0	2.2	
	320	1	6		16.1	9.3	
Control (pH 5.5)		55			1.6		
$Na_2Cr_2O_7$ (pH 5.5)	5	56			0.8		
	20	55			2.5		
	80	40			7.4		
	320	1			55.0		
$Na_2Cr_2O_7$ (pH 7.0)	0	60			0.5		
	5	60			1.4		
	20	58			2.7		
	80	29			9.6		
	320	1			57.0		
$Cr_2(SO_4)_3$ (pH 5.5)	5	58			1.3		
	20	56			1.4		
	80	52			2.4		
	320	25			2.8		

[a] Crops were grown in the amended soils in three different ways: (1) crop was grown for 7 weeks in soil immediately after amendment; (2) soil with amendment was incubated in a moist chamber for 21 weeks prior to planting crop (7-week growth period); (3) soil with amendment was incubated for 36 weeks prior to planting crop (7-week growth period).

Source: Adapted from Mortvedt and Giordano, 1975*b*, Tables 2, 3, and 7, pp. 171-173. Reprinted by permission of the publisher.

contribute trivalent chromium in oxide form or hexavalent chromium as either chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$). In the presence of organic matter, hexavalent chromium would be reduced to trivalent chromium and would either precipitate as the hydroxide, carbonate, or sulfide; trivalent chromium would adsorb on clays, iron oxides and hydrous oxides, and organic matter. Chromates are rare in nature and are stable only in alkaline, oxidizing conditions (Allaway, 1968). The adsorption phenomenon may be the main mechanism of retention in dilute soil solutions (Murrmann and Koutz, 1972). Jenne (1968) presented arguments for the significance of hydrous iron and manganese oxides in the binding of manganese, iron, cobalt, nickel, copper, and zinc in soils, and Baker (1973) argued for the significance of soil organic matter. Although chromium was not discussed in either of these publications, a similar binding may occur because chromium is in the same transitional series as these elements.

Prince (1957*a*, 1957*b*) used spectrographic analyses to study the relationship between trace element concentrations in corn and ragweed and in the soil in which they were grown. Chromium concentrations in corn were not closely related to soil chromium concentrations; however, ragweed chromium concentration did increase with soil chromium concentration (Table 4.4). Since chromium values in corn decreased with age of the leaf, uptake over a period of time was not constant. Data on the relationship between available chromium in the soil and chromium concentrations in the root of corn would be more valuable information because chromium is not usually translocated (Section 4.2.3).

Table 4.4. Chromium concentrations in ten New Jersey soils and in corn and ragweed grown on these soils (ppm)

Soil type	Soil	Corn leaves			Ragweed
		Young	Tassel stage	Mature	
Annandale loam	32			1.37	
Collington sandy loam	20			1.69	
Coltz loam	40	1.13	0.84	0.47	2.74
Cossayuna loam	20	0.74	0.69	0.44	1.31
Croton silt loam	38			2.18	
Lansdale loam	30			1.61	
Norton loam	75	1.84	1.15	0.80	6.77
Sassafras sandy loam	45	2.07	1.22	0.50	4.90
Squires loam	46			1.28	
Washington loam	39	0.88	1.16	0.68	4.09

Source: Adapted from Prince, 1957*a*, Tables 5-7, pp. 402-404, and Prince 1957*b*, Tables 1 and 3, pp. 414-415. Reprinted by permission of the publisher.

No information was found relating soil organic matter to plant uptake. Both dichromate and chromate ions are oxidizing agents which, when discharged onto soils, would oxidize organic matter (Section 2.2.5). Also, an increased soil organic content generally allows for both increased adsorption and increased cation-exchange capacity. Therefore, an increased organic content might be expected to allow more available chromium to be retained within the soil. The organic content could be of particular importance in serpentine soils, which are characterized by high chromium and nickel contents in addition to a low calcium to magnesium ratio.

Few reports have emphasized the relationship between soil pH and chromium uptake. Most metals are more soluble at low pH values (pH 4 to 5) and, thus, are more available for uptake than at high pH values (pH 7 to 8). For landfills, pH should be maintained at 6.5 or above (Chaney, 1973). While chromium, like other metals, is considered to be more available at lower pH values (Murrmann and Koutz, 1972), Patterson (1971) has shown that uptake of both trivalent and hexavalent chromium into barley roots increased with an increase in soil pH from 5.6 to 7.8. Injury, however, only occurred with hexavalent chromium. No explanation for this apparent contradiction was presented.

Interactions occurring between various elements within the soil can affect the exchangeable and soluble soil concentrations of a particular element (Black, 1968). No specific data were found for interactions between chromium and other elements in the soil.

Interactions among elements can affect their concentrations in and toxicity to the plant. The only data found for chromium were those of Wallace, Sufi, and Romney (1971), who studied the effects of calcium and chelating agents on heavy metal concentrations in bush beans grown in solution cultures. Increasing calcium concentrations decreased the toxic effect of 10^{-4} *M* chromium (as measured by decreased wet weight). Addition of ethylenediaminetetraacetic acid (EDTA) to the optimum calcium concentration restored the toxic effect of chromium. No specific mechanisms have been proposed for the observed interactions among calcium, EDTA, and chromium.

4.2.3 Translocation

The fate of absorbed chromium in plants is unknown. Soluble organic complexes of some trace elements have been observed within plants (Tiffin, 1972), but the only report for chromium has been by Lyon, Peterson, and Brooks (1969*a*, 1969*b*) in experiments with *Leptospermum scoparium*. The xylem exudate from both roots and shoots of plants cultured in ^{51}Cr-labeled $NaCrO_4$ solutions contained only chromate, while the 80% ethanol extract of root, leaf, and stem contained three chromium complexes, one of which was identified as the trioxalatochromate ion. Most of the ^{51}Cr was found in the root (267 counts min^{-1} mg^{-1} dry wt in shoots; 17,300 counts min^{-1} mg^{-1} dry wt in roots). Thus, hexavalent chromium was absorbed by the plant but little was transported in the xylem to the shoot. The site of complexation was not determined. Myttenaere and Mousny (1974) also showed in rice that little radiochromium [supplied to the roots as either chromium(III) or $CrO_4{}^{2-}$] was transported to the shoots. If chromium was supplied to the roots as chromium-EDTA, less total absorption occurred; however, significant amounts were transported to the leafy shoots. Similar results were found for rice by Verfaillie (1974) (Table 4.2). DeKock (1956) failed to find significant chromium concentrations in the leaves and stems of mustard plants exposed to solutions containing 2 ppm chromium. He also observed that the chromium content of roots was less when chromium was supplied in the chelated form.

Chromium-51-labeled trivalent or hexavalent chromium supplied for 14 days was taken up by both flowering wheat and bean plants (Huffman and

Allaway, 1973*a*). At maturity, the wheat roots contained 95% of the hexavalent chromium and 96% of the trivalent chromium; bean roots contained 93% of the hexavalent form and 92% of the trivalent form (Table 4.5). Thus, chromium was not significantly translocated from the root to the shoot of the plants studied.

Table 4.5. Distribution of ^{51}Cr in wheat and beans grown in solution culture with either ^{51}Cr labeled trivalent or hexavalent chromium

Plant tissue	Bean				Wheat			
	Cr(VI)		Cr(III)		Cr(VI)		Cr(III)	
	(ng/g)	(% total Cr)	(ng/g)	(% total Cr)	(ng/g)	(% total Cr)	(ng/g)	(% total Cr)
Seed	3	0.03	2	0.02	1	0.1	1	0.1
Chaff (pods)	32	0.5	50	0.9	18	0.9	16	1.1
Stems	26	1.1	37	1.5	21	3.0	15	1.7
Leaves	144	5.1	166	6.5	74	1.1	64	1.4
Roots	3791	93.2	3096	91.5	5378	94.9	3982	95.7

Source: Adapted from Huffman and Allaway, 1973*a*, Table II, p. 984. Reprinted by permission of the publisher.

Levi, Dalschaert, and Wilmer (1973) observed little translocation in bean and lettuce of foliarly applied ^{51}Cr (drop or spray methods) added as either $CrCl_3$ or Na_2CrO_4. Although slightly greater amounts of activity were exchanged with the carrier when chromium was added as Na_2CrO_4, the increase did not exceed 7% of the total. The results indicated that most of the added trivalent and hexavalent chromium was retained within the tissue in an unexchangeable form. No data were presented to show that chromium was retained in the hexavalent form within the tissue.

Data for plants growing on serpentine soil (Section 4.2.4.2.1) showed that chromium is mainly concentrated in subterranean parts, although some high values given for aerial parts indicate that some translocation occurs (Lounamaa, 1956).

The subcellular localization of chromium and its exact chemical form within the cell have not been adequately characterized. Schroeder, Balassa, and Tipton (1962) reported trivalent and hexavalent content of dry-ashed plant material and found species variations (Table 4.6). The assumption that the oxidation state is unchanged during dry ashing is very hazardous and the differences are as likely to represent minor changes in ashing conditions as they are the original chromium chemistry.

When rice plants were grown in nutrient solutions containing low levels of chromium (0.073 ppb trivalent chromium, 0.075 ppb CrO_4^{2-}) and subjected to a sequential extraction procedure, protoplasmic fractions contained 84.50% of the label when trivalent chromium was added and 92.81% of the

Table 4.6. Trivalent and hexavalent chromium in the ash of some plant materials

Plant sample	Chromium content (μg/g wet wt)			Cr(III) (%)
	Cr(III)	Cr(VI)	Total	
Thyme	3.38	0.41	3.79	89.4
Black pepper	1.02	1.24	2.26	45.1
Tomato, raw			0.01	
Maple leaves	0.14	0.03	0.17	82.3
Red oak leaves	0.03	0.05	0.08	37.5
Pine needles	0.14	0.07	0.21	66.7

Source: Adapted from Schroeder, Balassa, and Tipton, 1962, Table 9, p. 959. Reprinted by permission of the publisher.

label when CrO_4^{2-} was added. The cell wall fractions contained 15.50% of the trivalent chromium and 7.19% of the CrO_4^{2-} (Myttenaere and Mousny, 1974). Although this experiment showed that chromium supplied as either trivalent or hexavalent chromium will ultimately enter the cell, no information on whether CrO_4^{2-} was reduced prior to uptake was given.

Data from the cellular fractionation of bean and wheat plants previously incubated in ^{51}Cr-labeled hexavalent chromium solutions are given in Table 4.7 (Huffman and Allaway, 1973*b*). The most notable difference between the data for wheat and for bean was the chromium content of the 0.2 *N* HCl extract of the root. The authors suggested that most of the chromium in wheat may have been in a soluble, and hence, acid-extractable form (perhaps in the vacuole), while bean root may have retained the chromium in an insoluble form in the cell walls. However, distribution in the various subcellular fractions from differential centrifugation of plant homogenates (Table 4.8) showed most of the activity in the supernatant fraction (homogenization). Since the cell walls were probably largely pelleted, most chromium was apparently not in the cell wall fraction. The results obtained by the extraction and fractionation procedures apparently differed considerably. Analysis of the fractionation supernatant from bean leaves gave one peak with gel permeating chromatography (Sephadex G-10) and with paper electrophoresis, but this peak did not coincide with known standards of chromium citrate, chromium aconitate, chromium oxalate, or chromate. Preliminary work indicated that the chromium was present predominantly as an anionic complex with a low molecular weight. Blincoe (1974) identified chromium in lucerne as an anionic complex with a molecular weight of about 2900.

Table 4.7. Chromium-51 extracted by various methods from wheat and beans grown in solution culture with ^{51}Cr-labeled hexavalent chromium[a] (percent)

Plant	80% ethanol	Ether	Boiling water	0.2 *N* HCl	Acetone precipitate from HCl-soluble	0.5 *N* $HClO_4$	Acetone precipitate from $HClO_4$-soluble	2 *N* NaOH	Residue
Wheat									
Grain	49								
Chaff	9	2	24	31	2	18	3	5	6
Stems	16	0	67	5	3	1	2	3	4
Leaves	4	0	47	29	1	12	0	5	2
Roots	3	0	9	58	1	9	1	14	4
Bean									
Grain	41								
Pods	10	1	42	17	4	10	1	6	9
Stems	22	2	28	17	4	18	1	4	4
Leaves	16	0	39	25	1	12	0	4	3
Roots	5	1	6	2	0	13	1	37	34

[a] Extractions were done sequentially from dried materials.

Source: Adapted from Huffman and Allaway, 1973*b*, Table III, p. 984. Reprinted by permission of the publisher.

Table 4.8. Distribution of ^{51}Cr in various subcellular fractions after differential centrifugation of leaf homogenates

Plant	Treatment	Chromium-51 in fraction (%)[a]			
		Nuclei and debris	Mitochondria	Microsome	Supernatant
Wheat	Cr(III)	3	2	1	89
	Cr(VI)	4	2	1	87
Bean	Cr(III)	4	4	2	79
	Cr(VI)	4	3	1	86

[a] Values do not add to 100% because pellet washings were not recombined.

Source: Adapted from Huffman and Allaway, 1973*a*, Table IV, p. 985. Reprinted by permission of the publisher.

Apparently, significant amounts of chromium can be moved into tissues in certain instances. A single application of Elgetol, a blossom thinner containing 4,6-dinitro-*o*-cresol and 1.9% sodium bichromate, to apple trees at blossom led to high chromium contents in the young fruit (about 0.34 μg/g two weeks after application) (Coahran, Maxwell, and Zucker, 1973). Although the tissue chromium concentration in both treated and untreated trees dropped during the 19 weeks of fruit development due to growth of the fruit, the total amount of chromium in the apple fruit increased considerably in both treated and untreated trees. Thus, in apple development, chromium appeared to be transported to the fruit in measurable amounts and this chromium flow was apparently a normal physiological process. The authors suggested that the soil was the source of the chromium which flowed to the fruit.

4.2.4 Distribution

The concentration of chromium found within a plant depends on the type of plant and the chromium content of the soil. In general, chromium concentrations in soil range from 5 to 3000 ppm, with a mean of 100 ppm (Bowen, 1966) (Section 7.3.3). Chromium concentrations in the plant could range from <1 to >3000 ppm (Lounamaa, 1956), but the more normal range would be 0.2 to 1.0 ppm (Allaway, 1968). Allaway (1968) stated that chromium is not concentrated at any stage in the cycle from soil to plant to animal, but data are inadequate to support this generalization. Since few studies on the available chromium content of soils have been reported, bioaccumulation of chromium in plants is difficult to assess.

4.2.4.1 Crop Plants — Few data were found on chromium concentrations in crop plants. Chromium concentrations on a wet weight basis, given by Schroeder, Balassa, and Tipton (1962) for various food plants, suggest that most crop species have similar chromium levels (0 to 0.09 ppm), although radishes and parsnips (root crops) have somewhat elevated levels (Table 4.9).

Table 4.9. Chromium concentrations in food plants

Plant sample	Chromium content (ppm wet wt)
Vegetables	
Potato, white	0.0
Beans, dried, navy	0.08
Beans, dried, yellow-eye	0.05
Beans, wax	0.03
Beans, green string	0.02
Lentils, dried	0.09
Beets	0.01-0.03
Radishes	0.0
Parsnips	0.13
Parsnip leaves	0.08-0.19
Turnip leaves	0.04-0.06
Carrots	0.0-0.03
Onions	0.01-0.02
Spinach	0.0-0.05
Swiss chard	0.06
Squash, summer	0.02
Cucumber	0.01-0.03
Kohlrabi	0.0
Cauliflower	0.02
Cabbage	0.01-0.06
Sauerkraut	0.03
Rhubarb, raw	0.02
Lettuce, garden	0.07
Lettuce, head	0.02-0.13
Fruits	
Peach, Elberta, raw	0.01
Raisins	0.02
Blackberries, wild	0.0
Tomato, raw	0.01
Apple, MacIntosh	0.02
Pear	0.01
Plum	0.02
Grains and cereals	
Corn, fresh on cob	0.02
Corn meal	0.05
Rye, seed	0.05
Rye, whole	0.04
Wheat, whole (Japanese)	0.08
Rice, (Japanese) 204 samples	0.04
Rice	0.05
Oatmeal, dry	0.06

Source: Adapted from Schroeder, Balassa, and Tipton, 1962, Table 6, p. 949. Reprinted by permission of the publisher.

Since chromium is not translocated to any great extent, the roots of these food plants might be expected to have higher chromium concentrations than other plant parts.

Trace elements within grains may be concentrated in germ (Lillehoj, Garcia, and Lambrow, 1974). Data for chromium showed that whole kernel corn contained 0.075 ppm chromium, while germ contained 1.43 ppm chromium. The amounts of trace elements present also influenced the production of aflatoxin by *Aspergillus flavus* infections of corn (Section 3.3.3). Data from several other studies, summarized by Pratt (1966), illustrate that a broad range of concentrations can be found among different plant species (Table 4.10). Although these data give an overall view of chromium concentrations in plants, they are of limited value unless available chromium concentrations in soils are determined and the usual analytical uncertainty also limits their utility.

Table 4.10. Chromium concentrations in crop plants

Plant	Tissue	Growth stage	Conditions	Chromium concentration (ppm dry wt)
Barley	Leaves			7.6
Cherry	Fruit	Mature		0.032
Corn	Leaves	Young		0.74-2.07
	Leaves	Tassel		0.69-1.22
	Leaves	Mature		0.50
	Stalks	Mature		0.22
	Grain	Mature		0.48
	Cobs	Mature		0.53
	Husks	Mature		0.34
Oat	Leaves and stem		Growing on serpentine soil	3.0-11.0
Orange	Leaves		Greenhouse	0.2-0.3
	Leaves		Field	10.0
	Leaves	Seedling		0.50-1.00
Pear	Whole fruit	Mature		0.03
	Pericarp	Mature		0.50
	Peel	Mature		0.85
Potato	Tuber			0.002
Wheat	Leaves			4.5-14.8

Source: Adapted from Pratt, 1966, Table 1, p. 138.

4.2.4.2 Noncrop Plants

4.2.4.2.1 Serpentine soil flora — Serpentine soils, which overlie serpentine rocks, are characterized by high concentrations of chromium, nickel, and cobalt; a high magnesium to calcium ratio; and a deficiency of other essential plant elements such as phosphorus, potassium, and molybdenum. They are typically unproductive as farm or timberland but do support endemic species with distinct ecotypes (Whittaker, 1954). In the United States, major serpentine areas occur in the Appalachian chain from western Massachusetts to Georgia and along the Pacific Coast mountain ranges in California, Oregon, and Washington (Whittaker, 1954). The specific cause of the infertility of serpentine soils is unknown and it may vary from site to site.

A wide range of chromium concentrations can be found in plants growing on serpentine soils (Lounamaa, 1956; Lyon et al., 1970, 1971). Table 4.11 illustrates the variability among species. Some plants take up chromium in an amount roughly proportional to total soil chromium concentration (for example, *Leptospermum scoparium*), while others apparently can exclude chromium (for example, *Phyllocladus alpinus*). Lack of apparent correspondence between plant and soil chromium concentrations for some other species may be due to the difficulty of determining the available chromium content in the specific soil near the plant.

In a study of shrubs growing on high nickel-chromium soils, Cole (1973) showed no shrub species to contain high chromium amounts and suggested that most species are able to restrict chromium entry. For example, the nickel accumulator *Hybanthus floribundus* did not contain high levels of chromium (0.04 to 12 ppm chromium, dry wt basis).

Additional data on chromium concentrations in plants growing on high chromium soils are discussed in the next section.

4.2.4.2.2 Herbaceous and woody plants — The most comprehensive study of the relationship between trace element composition of plants and the type of rock in the substratum was made by Lounamaa (1956) in Finland. Lichens, mosses, ferns, conifers, deciduous trees and shrubs, dwarf shrubs, and grasses and herbs were examined. Table 4.12 gives chromium concentrations in soils and rocks of Finland. Ultrabasic rocks and the soils overlying them contained the highest chromium concentration. Chromium concentrations in plants growing on these rocks and soils are given in Tables 4.13 and 4.14. Chromium concentrations were lower in plants than in corresponding soils and rocks, although relatively high chromium concentrations were found in plants growing on ultrabasic rock and soil. Subterranean plant parts had higher concentrations than aboveground parts, again suggesting that chromium is not easily translocated throughout the plant.

No other comprehensive studies of the relationship between the plants and soils were found. Chromium concentrations in a variety of plants are given in Table 4.15. In the various groups analyzed, concentrations ranged from undetectable amounts to 27 ppm chromium (*Aspergillus microcysticus*); the typical range was from 0.2 to 5.0 ppm chromium (dry wt basis). Ewing, Howes, and Price (1969) determined concentrations of several trace elements in fruits and vegetables from Panama (Table 4.16). The range observed for chromium (0.003 to 8.0 ppm) is similar to that found in other studies.

The chromium content of a variety of plant foods has been determined by several research groups (Section 8.3). The reported range of chromium concentrations in edible portions of these plants was similar to that found in

Table 4.11. Chromium concentrations in plant and soil samples from a serpentine area

Chromium concentration in soil (ppm)	Plant species	Chromium concentration in plant sample (ppm of ash)
150	*Cassinia vauvilliersii* var. *serpentina*	370
	Leptospermum scoparium	210
	Coprosma parviflora	120
	Dracophyllum filifolium var. *collinum*	300
	Metrosideros umbellata	20
	Podocarpus totara	80
	Lichen (species unknown) on rock	34,000
930	*L. scoparium*	1,100
	Myosotis monroi	3,500
	D. pronum	4,400
	Hymenanthera alpina	70
	Myrsine divaricata	125
	Stellaria roughii	3,600
5,300	*Pimelea suteri*	3,200
62,000	*Cassinia vauvilliersii* var. *serpentina*	4,600
	Hebe odora	8,500
	L. scoparium	9,000
	Gentiana corymbifera	5,400
	Phormium colensoi	700
4,200	*H. odora*	380
	L. scoparium	840
	Myosotis monroi	2,000
	Notothlaspi australe	1,300
	Hymenanthera alpina	1,200
7,600	*C. vauvilliersii* var. *serpentina*	60
	Coprosma parviflora	740
	Nothofagus solandri var. *cliffortioides*	36
	Phyllocladus alpinus	52
3,800	*Cassinia vauvilliersii* var. *serpentina*	13
	Hebe odora	13
	Coprosma parviflora	44
	N. solandri var. *cliffortioides*	36
	P. alpinus	20
1,500	*C. cunninghamii*	60
	Dacrydium biforme	44
	Myrsine divaricata	52
	N. solandri var. *cliffortioides*	44
	P. alpinus	20
500	*C. banksii*	52
	C. cunninghamii	52
	D. biforme	36
	N. menziesii	28
	P. alpinus	13
23,000	*H. odora*	36
	L. scoparium	3,800
	Myosotis monroi	460
4,900	*Cassinia vauvilliersii* var. *serpentina*	1,500
	H. odora	1,000
	L. scoparium	700
	Dracophyllum uniflorum	2,900
	Lycopodium australianum	7,700

Table 4.11 (continued)

Chromium concentration in soil (ppm)	Plant species	Chromium concentration in plant sample (ppm of ash)
21,000	*C. vauvilliersii* var. *serpentina*	360
	H. odora	105
	Leptospermum scoparium	2,300
	M. monroi	600
	D. filifolium var. *collinum*	300
	Myrsine divaricata	580
5,000	*C. vauvilliersii* var. *serpentina*	2,700
	H. odora	1,150
	Notothlaspi australe	200
	Anisotome aromatica	115
8,200	*H. odora*	1,500
	L. scoparium	4,100
	G. corymbifera	400
	Hymenanthera alpina	6,000
3,200	*C. vauvilliersii* var. *serpentina*	2,200
	Hebe odora	90
	L. scoparium	650
	G. corymbifera	780
	M. divaricata	850
	S. roughii	350

Source: Adapted from Lyon et al., 1970, Table 2, pp. 136-137. Reprinted by permission of the publisher.

Table 4.12. Chromium content of major rock types in Finland and of the soils formed over these rocks

Rock type	Chromium content (ppm)			
	Rock		Soil	
	Mean	Range	Mean	Range
Silicic	87 ± 14	<3-1000	140 ± 18	10-300
Ultrabasic	2200 ± 260	300-6000	4000 ± 310	2000-6000
Calcareous	380 ± 98	<3-3000	110 ± 23	<3-300

Source: Adapted from Lounamaa, 1956, Table 3, pp. 52-53. Reprinted by permission of the publisher.

Table 4.13. Chromium concentrations in plants growing in soils overlying silicic, ultrabasic, or calcareous rocks

Plant	Tissue	Chromium concentration (ppm of ash)					
		Plants growing on silicic rock		Plants growing on ultrabasic rock		Plants growing on calcareous rock	
		Mean	Range	Mean	Range	Mean	Range
Lichens		39 ± 6	10-300	650 ± 160	300-1000		
Mosses		48 ± 18	10-100	200 ± 45	100-300	23 ± 7	10-30
Ferns	Frond	7 ± 1	<1-30	230 ± 90	10-1000	6 ± 2	3-10
	Subterranean parts	55 ± 13	1-300	740 ± 270	100-3000	120 ± 64	10-300
Conifers	Needles	7 ± 2	<1-60	18 ± 5	3-60	4 ± 1	<1-10
	Twigs	12 ± 2	<1-60	25 ± 10	1-100	10 ± 4	<1-30
Deciduous trees and shrubs	Leaves	5 ± 1	<1-30	26 ± 9	1-100	4 ± 1	<1-10
	Twigs	6 ± 1	<1-60	26 ± 9	3-100	3 ± 1	<1-10
Dwarf shrubs	Leaves	7 ± 1	<1-30	73 ± 32	3-300	11 ± 7	1-80
	Stems	17 ± 4	3-100	160 ± 68	3-600	25 ± 13	3-60
Herbs	Inflorescences	12 ± 5	<1-100	160 ± 47	3-600		
	Leaves	6 ± 3	<1-60	160 ± 72	3-1000		
	Stems	7 ± 2	<1-30	60 ± 21	3-300		
	Subterranean parts	31 ± 8	<1-100	910 ± 260	30-3000		
Grasses	Inflorescences	9 ± 3	<1-30	62 ± 23	3-300		
	Leaves and stems	9 ± 3	1-30	46 ± 12	3-100		
	Subterranean parts	87 ± 30	3-300	420 ± 99	3-1000		

Source: Adapted from Lounamaa, 1956, Tables 5, 8, 10, 14, 22, 28, 34, and 36, pp. 64-65, 70-71, 80-81, 98-99, 118-119, 132-133, 160-161, and 168-169. Reprinted by permission of the publisher.

Table 4.14. Chromium concentrations in selected plant species growing on different soils in Finland

Plant species	Chromium concentration (ppm of ash)
Lichens	
Peltigera canina	6-30
Cladina alpestris	10-1,000
Stereocaulon paschale	10-300
Parmelia centrifuga	200-10,000
Parmelia saxatilis	
Mosses	
Tortella tortuosa	10-300
Rhacomitrium lanuginosum	100-300
Hylocomium splendens	10-100
Ferns	
Woodsia ilvensis	3-30
Cystopteris fragilis	3-300
Lastrea phegopteris	3-300
Asplenium trichomanes	1-100
Asplenium septentrionale	1-1,000
Polypodium vulgare	1-300
Conifers	
Picea abies	1-100
Pinus silvestris	1-60
Juniperus communis	1-30
Deciduous trees and shrubs	
Populus tremula	3
Betula verrucosa	1-60
Almis incana	1-30
Rosa majalis	100
Sorbus aucuparia	1-30
Daphne mezereum	3-100
Lonicera xylosteum	1-10
Dwarf shrubs	
Vaccinium vitis-idaea	1-100
Calluna vulgaris	1-100
Empetrum nigrum	3-600
Grasses and herbs	
Molinia coerulea	3-60
Festuca ovina	3-100
Deschampsia caespitosa	3-100
Allium schoenoprasum	1-10
Polygonatum odoratum	1-60
Rumex acetosella	1-10
Viscaria vulgaris	1-300
Dianthus superbus	3-100
Sedum telephium	1-1,000
Saxifraga granulata	1-10
Rubus idaeus	1-30
Vicia cracca	10-100
Thymus serpyllum	3-100

Source: Adapted from Lounamaa, 1956, Tables 4, 7, 9, 13, 17, 26, and 31, pp. 60-61, 69, 74-78, 92-96, 106-112, 128-130, and 142-154. Reprinted by permission of the publisher.

Table 4.15. Chromium concentrations in a variety of plants

Species	Chromium concentration (ppm)		Reference
	Dry wt	Ash wt	
Algae			
Anacystis nidulas	1.2		Horovitz, Schock, and Horovitz-Kisimova, 1974
Aphanizomenon flos-aquae	9		
Laminaria saccharina	6		
Ahnpheltia plicata	2.9		
Caulerpa prolifera	11		
Chara fragilis	0.82		
Fungi			
Aspergillus microcysticus	27		Horovitz, Shock, and Horovitz-Kisimova, 1974
Hypoxylon fragiforme	0.65		
Alcuria aurantia	2.7		
Bulgaria inquinans	1.1		
Elaphomyces granulatus	0.43		
Clavulina cinerea	1.1		
Stereum hirsutum	3.3		
Lycoperdon pyriforme	3.0		
Scleroderma verucosa	9		
Lichens			
Cladonia retipora	4.6		Horovitz, Shock, and Horovitz-Kisimova, 1974
Mosses			
Marchantia polymorpha	1.0-14		Horovitz, Shock, and Horovitz-Kisimova, 1974
Sphagnum acutifolium	7		
Polytrichum commune	2.5		
Hypnum cupressiforme	8		
Hypnum cupressiforme	5-14.0		
Ferns and fern allies			
Psilotum triquetrum	0.27-0.97		Horovitz, Shock, and Horovitz-Kisimova, 1974
Selaginella willdenowii	0.43		
Lycopodium circinatum	0.33-0.59		
Equisetum giganteum	0.45		
Ophioglossum pedunculosum	0.45		
Salvinia auriculata	1.0-4.4		
Gymnosperms and angiosperms			
Encephalartos lehmanii	0.05-0.53		Horovitz, Shock, and Horovitz-Kisimova, 1974
Ginkgo biloba	0.20		
Juniperus communis	0.37-0.64		
Ephedra gerardiana	0.45-0.56		
Liriodendron tulipifera	0.37		
Pulmonaria saccharata	0.43		
Elodea canadensis	0.43		
Carex pendula	0.12		
Prunus serotina (wild cherry) leaves	0.57	7.9	Schroeder, Balassa, and Tipton, 1962
Betula papyrifera (white birch) leaves	0.19	3.2	
Fagus grandifolia (beech) leaves	0.29	5.6	
Acer rubrum (red maple) green leaves	0.11	1.8	
Acer rubrum (red maple) red leaves	0.20	3.2	
Quercus rubra (red oak) leaves	0.17	9.2	
Quercus rubra (red oak) acorns	0.02	0.9	
Thuja occidentalis (arborvitae) leaves	0.35	6.7	
Thuja occidentalis (arborvitae) buds		0.0	
Pyrus americana (ash) leaves	0.70	7.7	
Populus tremuloides (quaking aspen) leaves	0.25	4.0	

Table 4.15 (continued)

Species	Chromium concentration (ppm)		Reference
	Dry wt	Ash wt	
Gymnosperms and angiosperms			
Pyrus malus (apple) leaves	0.33	3.2	Schroeder, Balassa, and Tipton, 1962
Pyrus malus (apple) apples	0.13	5.9	
Pinus strobus (white pine) needles	0.49	15.8	
Juniperus communis berries	0.49	14.5	
Picea rubra (spruce) needles	0.24	6.9	
Trifolium repens (clover) shoot	0.34	2.3	
Medicago sativa (alfalfa) shoot	0.09	1.0	
Dactylis glomerata (pasture grass) shoot	1.30	22.5	
Quercus palustris (pin oak) leaves	3.8 ± 0.8		Smith, 1973
Quercus palustris (pin oak) twigs	2.8 ± 0.4		
Acer saccharum (sugar oak) leaves	1.9 ± 0.3		
Acer saccharum (sugar oak) twigs	2.3 ± 0.2		
Acer platanoides (Norway maple) leaves	2.8 ± 0.2		
Acer platanoides (Norway maple) twigs	1.6 ± 0.1		
Tsuga canadensis (hemlock) leaves	2.8 ± 0.4		
Tsuga canadensis (hemlock) twigs	3.5 ± 0.4		
Taxus spp. (yew) leaves	3.9 ± 0.3		
Taxus spp. (yew) twigs	6.0 ± 1.4		
Picea abies (spruce) leaves	2.6 ± 0.4		
Picea abies (spruce) twigs	4.9 ± 0.4		
Acer rubrum (red maple) leaves	0.27–0.38		Hanna and Grant, 1962
Acer saccharinum (silver maple) leaves	0.27		
Acer saccharum (sugar maple) leaves	0.38		
Fagus grandifolia (beech) leaves	0.26		
Ilex opaca (holly) leaves	0.06–0.37		
Kalmia latifolia (mountain laurel) leaves	0.08–0.62		
Pieris japonica (heath) leaves	0.01–0.60		
Pinus strobus (white pine) leaves	0.25–2.4		
Platanus occidentalis (sycamore) leaves	0.23		
Quercus palustris (oak) leaves	0.10–0.58		
Rhododendron roseum leaves	0.06–0.38		
Tsuga canadensis (hemlock) leaves	0.37–0.56		
Triticum spp. (wheat) seed	0.003–0.043		Welch and Cary, 1975
Aloe spp.		17	Baumslag and Keen, 1972
Amaranthus spp.		38	
Juniperus virginiana (cedar)	1.8–4.5		Connor, Shacklette, and Erdman, 1971

both crop and wild plants. However, the relative biological value of chromium in foods used for animal nutrition was not necessarily related to the chromium concentration in the food (Toepfer et al., 1973).

4.2.4.2.3 Water plants — Little information was found on the chromium concentrations in water plants. Fukai and Brokey (1965) found that the marine taxa *Zostera* sp. and *Posidonia oceanica* (eelgrass) contained 4.2 ppm and an average of 1.6 ppm chromium on a dry weight basis, respectively.

Table 4.16. Chromium content of fruits and vegetables from Panama

Fruit	Chromium content (ppm dry wt)
Plantain, dried	0.1-1.2
Banana	0.1-0.5
Breadfruit	2.0
Sugarcane	0.7
Coconut	0.15
Cocoa beans	0.50
Avocado	0.003
Kidney beans	0.05
Rice	0.6
Corn	0.25
Yam (name)	0.1-0.2
Yam (otoe)	8.0
Cassava	0.15-1.5

Source: Adapted from Ewing, Howes, and Price, 1969, Table 3, p. 14.

4.2.5 Plant Concentration and Pollution Sources

One type of chromium pollution results from chromate present as a corrosion inhibitor in cooling towers and used, for example, with nuclear-powered steam generators and process facilities requiring closed cycle cooling (Taylor et al., 1975). Drift from these facilities transports chemicals to adjacent terrestrial areas and surface waters. Although similar species were not examined at each distance from the cooling towers in this study, chromium concentrations in grasses, forbs, trees, and litter decreased considerably with distance. Some contamination was evident at 1230 m (4000 ft) from the cooling tower (Figures 4.2 and 4.3). No information was given on whether increased amounts of chromium were due simply to surface deposition or to actual plant uptake.

A regional and historical study of the heavy metal content of the moss *Hynum cupressiforme* in Sweden showed that a small increase in chromium content occurred from 1870 to 1969 (5.8 to 7.7 ppm dry wt) in samples from the more industrialized areas (Ruhling and Tyler, 1969). Since moss generally obtains a large proportion of its mineral content from airborne particles, an increase in chromium air pollution can be inferred.

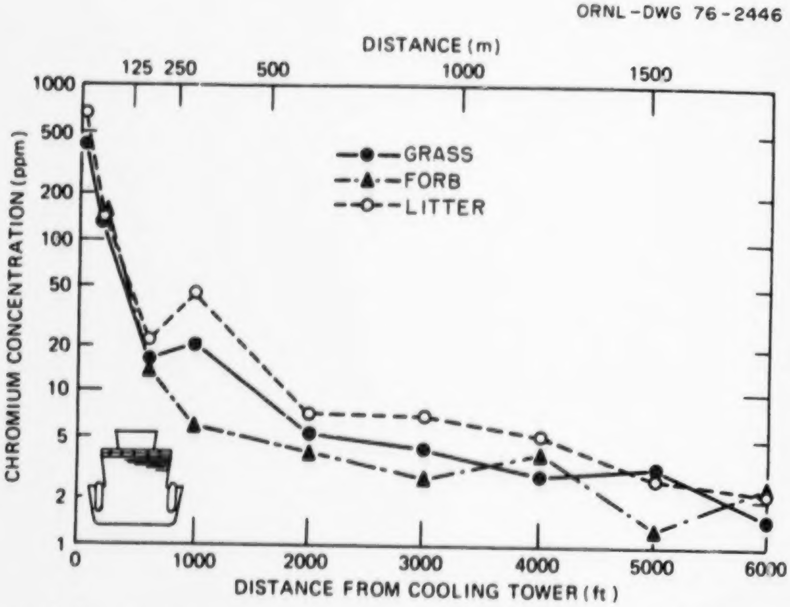

Figure 4.2. Chromium concentrations in vegetation illustrating the transfer of increased quantities of the trace element by cooling-tower drift to the landscape. Background concentrations (parts per million ± 1 standard error) were: grass, 0.40 ± 0.03; forb, 0.65 ± 0.05; litter, 2.65 ± 0.74. Source: Adapted from Taylor et al., 1975, Figure 3, p. 414.

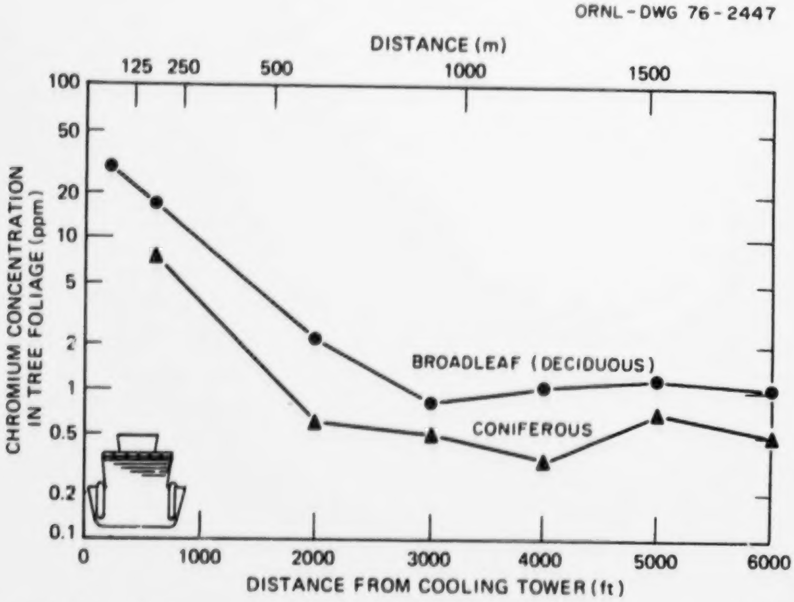

Figure 4.3. Chromium concentrations in foliage of deciduous and coniferous tree species. Background concentrations (parts per million ± 1 standard error) ranged from 1.32 ± 0.42 for deciduous broadleafs to 1.25 ± 0.30 for conifers. Source: Adapted from Taylor et al., 1975, Figure 4, p. 415.

Although total and available chromium amounts within sludge-amended soils have been reported, there are few reports on the chromium content of plants grown in these soils (Page, 1974). The chromium data of LeRiche (1968) had certain anomalies (Table 4.17), the most striking of which was that chromium concentrations were higher in tops than in roots. Although treated soils contained up to 17 times the chromium concentration of untreated soils, chromium concentrations in plants grown on the two soils were similar.

Sewage sludge application to soils increased the content of chromium (and other elements) in fodder rape. Application of sewage containing 176 ppm chromium (dry wt basis) to soil (background level 36.1 ppm chromium) at the rate of 7 metric tons dry matter per hectare every second year for 12 years increased the soil content to 61 ppm chromium and increased the fodder rape concentration from 2.6 ± 0.17 ppm to 4.1 ppm chromium (Andersson and

Table 4.17. Chromium concentrations in plants grown on control and sludge-amended soils[a]

Sample	Chromium concentration (ppm dry wt)			
	Control soil		Amended soil	
	Plot 4	Plot 8	Plot 3	Plot 39
Soil[b] (0.5 *N* acetic acid)	0.7	0.2	2.0	3.5
Leeks[b]	0.42	1.00	0.28	0.80
Globe beets[b]				
Tops	0.9	0.8	0.8	1.2
Roots	0.3	0.3	0.5	1.1
Potatoes[b]				
Tops	2.20	1.20	2.50	3.50
Roots	0.08	0.10	0.01	0.05
Soil[c] (0.5 *N* acetic acid)	1.5	0.33	1.8	3.4
Carrots[c]				
Tops	0.44	0.38	0.82	0.94
Roots	0.03	0.03	0.09	0.04

[a] Sludge applications discontinued after 1961.

[b] Samples taken from 1959 to 1961.

[c] Samples taken in 1967.

Source: Adapted from LeRiche, 1968, Tables 1-6, pp. 205-206. Reprinted by permission of the publisher.

Nilsson, 1972). However, lettuce grown on sewage-amended soils (80 and 160 metric tons added per hectare, containing 9.5 and 2 ppm of 0.5 acetic acid-extractable chromium) did not contain detectable chromium levels (Dudas and Pawluk, 1975).

Mortvedt and Giordano (1975*b*) showed that high chromium concentrations in sludge did not reduce yield of corn or increase tissue chromium concentrations, which suggests that most chromium in sludge is unavailable for plant uptake. Amounts of available chromium are usually very low because of the insoluble nature of most chromium compounds. The land disposal of municipal sludges may not result in a serious problem of chromium uptake into the food chain because the chromium is in the unavailable trivalent state. Other elements within the sludge present a greater problem. Chaney (1973) has discussed the important factors in soil retention of these elements (cadmium, zinc, copper, and nickel) and in their uptake by plants.

Small amounts of heavy metals are also supplied to the soil through application of commercial fertilizers. Mortvedt and Giordano (1975*a*) showed that plant uptake of chromium (and of other heavy metals with the exception of zinc) was not significantly increased with the usual application rates of phosphorus fertilizers. Plant uptake of heavy metals was lower on limed soil than on acid soil. Uptake of chromium did not increase even when $CrCl_3$ was added in rather high amounts to pots supplied with phosphorus additions of 200 and 600 mg/pot.

4.2.6 Elimination

No information on the bioelimination of chromium from living plant organs was found. Since a small, but measurable, quantity of chromium is translocated from root to shoot, small amounts could be lost from the plant by leaf, branch, fruit, and flower drop and by rain leaching. However, natural chromium is typically in an insoluble, immobile form; therefore, extensive leaching of chromium by rain would appear unlikely.

Studies concerned with the direct contamination of field plants with radioactive nuclides released from bomb tests or nuclear accidents have suggested that field plants lose chromium with time, which indicates elimination from the plants. A small amount of chromium, sprayed on barley as ^{51}Cr-labeled $Cr(NO_3)_3$, was absorbed by foliage and translocated to developing husks and grain. This translocation indicated that field loss occurs and is perhaps greatest in the earliest part of the growing season (Aarkrog and Lippert, 1971). Mechanisms of loss were not discussed; however, initial retention was related to the surface of the plant (where surface was defined as the ratio of dry weight to height). Thus, a portion of the activity was probably adsorbed or retained on the plant surface and never absorbed by the plant. Spraying ^{51}Cr-labeled Na_2CrO_4 on a grassland area gave similar results. A definite field loss of chromium occurred and a small amount of activity appeared in new growth after removal of the sprayed foliage (Chadwick and Chamberlain, 1970).

Fescue grass in a field was contaminated with radiolabeled sodium chromate to quantify the retention of simulated drift from a cooling tower

(Taylor, Gray, and Parr, 1976). All applied chromate was retained during the first week after application. Two rains during the second week removed about 50% of the initial deposition. By the fifth week, less than 5% remained, which suggested that contamination was primarily a surface phenomenon and that the contamination remained soluble. Drift-contaminated foliage and litter from the field plots were sampled and covered with distilled water to simulate six successive 1-in. rainfalls. Approximately 7% to 9% of the total chromium applied was removed from the foliage with each rainfall simulation, whereas only 3% was removed from the litter. These results suggest that chromium in litter is less soluble and not as easily removed by weathering phenomena.

4.3 EFFECTS

Studies on the effects of various chromium compounds (trivalent and hexavalent) in different concentrations on plant growth have centered on symptoms of toxicity; no studies providing information on molecular mechanisms or explanations for toxicity were found. The minimum chromium concentration required to produce visible symptoms varies for different species and depends on chemical form and a host of environmental factors affecting availability. In some cases, addition of chromium has been beneficial for plant growth and yield (Section 4.2.1); however, most of these reports were for field experiments. Studies with controlled culture experiments are necessary to clarify the question of possible beneficial responses.

4.3.1 Smelter Waste Toxicity

During the production of metallic chromium and other chromium compounds from chromite, considerable quantities of waste containing soluble chromates are disposed on land adjacent to the smelters. Revegetation of these areas is necessary after the smelters are abandoned. Examples reported were for smelters in Great Britain. In tests with *Sinapis alba*, Gemmell (1973) determined that the combined effects of high chromate concentration and high pH inhibited plant growth. As little as 1% of the unweathered wastes (in 99% sand) completely inhibited germination, while 0.02% reduced shoot growth by 50%. Weathered waste was about 10% as toxic as the unweathered waste. Breeze (1973) concluded that neither sand nor topsoil would be successful as a diluent in decreasing waste toxicity and that chemical detoxification methods would be necessary. Addition of $FeSO_4$ decreases toxicity of chromate wastes by reducing chromate to chromium(III) (which subsequently precipitates as Cr_2O_3) and/or by pH effects, depending upon the chemical composition of the substrate (Gemmell, 1972). For long-term success, however, additional revegetation methods are necessary because of the recurrence of metal toxicity on treated soils. Gemmell (1974) determined that covering the waste with a 25- to 30-cm layer of granular free-draining subsoil followed with top coverings of soil, peat, or sewage sludge was the best revegetation technique. Incorporation of $FeSO_4$ within the soil and subsoil should further aid in counteracting chromium toxicity.

4.3.2 Symptoms in Culture Experiments

Toxicity studies can be performed by treating plants in culture with a balanced mineral solution containing added chromium concentrations. Soybeans grown in nutrient culture (0 to 5 ppm hexavalent chromium) showed decreasing concentrations (and uptake) of calcium, potassium, phosphorus, iron, and manganese in shoots and of potassium, phosphorus, iron, and manganese in roots at culture levels as low as 0.5 ppm chromium (Turner and Rust, 1971). A significant decrease in fresh weight of tops occurred at 0.5 ppm chromium and of roots at 1.0 ppm chromium. Toxicity symptoms, which occurred at 5 ppm chromium, consisted of severe wilting of the tops. Soil pot culture experiments (0 to 6 ppm hexavalent chromium) showed similar decreasing trends in element content with increasing chromium content and similar toxicity symptoms. Death of plants occurred within three days of treatment with 30 and 60 ppm chromium. Plant chromium concentrations were not determined.

Bean plants cultured in nutrient solutions showed a reduction in leaf dry weight with as little as 0.01 ppm hexavalent chromium, but the greatest decrease in weight occurred in solutions containing from 0.1 to 1 ppm chromium (Rediske, Cline, and Selders, 1955). Root dry weight decreased at chromium concentrations greater than about 0.2 ppm. Hexavalent chromium apparently affects carbohydrate metabolism; both reducing sugars and sucrose amounts decreased with increasing hexavalent chromium concentrations. Additions of trivalent chromium to the nutrient medium produced increasing amounts of reducing sugars and sucrose in leaves. Protein nitrogen was not decreased significantly in either roots or leaves with concentrations of hexavalent or trivalent chromium (0.1 to 100 ppm). The primary visible symptom of chromium toxicity in bean plants was chlorosis; leaf chlorophyll concentration decreased with increased hexavalent chromium concentrations from 0.01 to 1 ppm (Rediske, 1956). Both iron and manganese uptake from nutrient solutions containing these chromium concentrations were reduced.

Sludge from municipal wastes was added to soils to supply up to 1360 ppm chromium. Chromium contained in these wastes did not affect yield (weight per pot) of corn (Table 4.3) (Mortvedt and Giordano, 1975*b*), whereas the addition of $Na_2Cr_2O_7$ to soils to give final chromium concentrations of 80 and 320 ppm decreased weight of corn plants by 87% and 97%. Addition of $Cr_2(SO_4)_3$ to 320 ppm in soil (pH 5.5) reduced yield by about 50%.

Tobacco and maize showed abnormal growth and development when grown in sand cultures containing various chromium concentrations (Soane and Saunder, 1959). At 5 and 10 ppm chromium (as $K_2Cr_2O_7$), intense stunting of tobacco plants occurred; 1 ppm chromium also inhibited stem elongation and inflorescence development. Severe root abnormalities led these authors to suggest that chromium had a "specially toxic effect on root development." However, since chromium is not translocated, it is difficult to estimate whether one tissue or organ is inherently more sensitive when it contains a particular chromium concentration.

Tobacco plants exposed to cooling-tower drift accumulated rather high levels of chromium at 15 m from the tower (Figure 4.4) (Parr, Taylor, and Beauchamp, 1976; Taylor et al., 1975). At distances farther from the cooling tower, accumulation was not as great. Tobacco was sensitive to increased chromium levels and showed about 75% reduction in leaf size or weight at 15 m and 200 m from the tower as compared to plants at 600 m and 1400 m (Figure

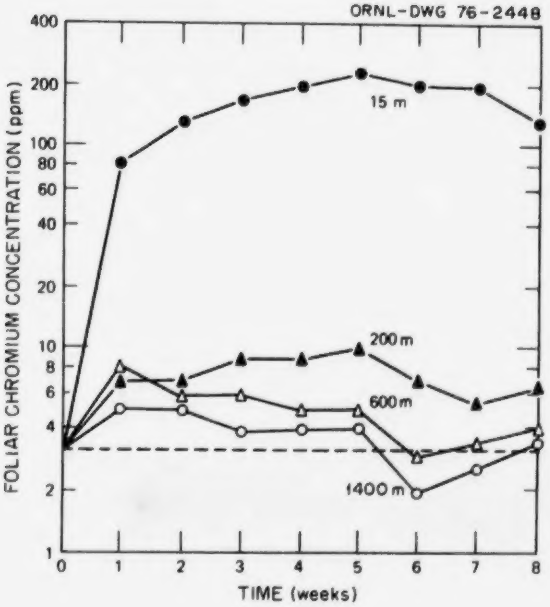

Figure 4.4. Accumulation of chromium by tobacco plants exposed to cooling-tower drift. Source: Adapted from Taylor et al., 1975, Figure 5, p. 417.

4.5). The inhibition to leaf growth at 200 m occurred at foliar concentrations of <10 ppm chromium, a value similar to the 5 ppm chromium shown to be toxic to tobacco by Soane and Saunder (1959).

Hunter and Vergnano (1953) observed that some oat plants grown in nutrient solutions in sand culture showed diffuse leaf chlorosis at 5 ppm hexavalent chromium; all plants were slightly chlorotic and stunted at 10 ppm. Root growth appeared normal at 5 and 10 ppm. At 25 and 50 ppm chromium, plants were stunted and had poor root development and brownish red necrotic areas on the leaves. Little chromium (0.4 to 3.9 ppm) was found in the leaves of plants cultured in 5 and 10 ppm chromium, but leaves cultured at 25 ppm contained 252 ppm chromium (dry wt). The authors reported that trace metals produced chlorosis in the following order: Ni > Cu > Co > Cr > Zn > Mo > Mn. However, Anderson, Meyer, and Mayer (1973) did not observe chlorosis in potted oats over a three-week period when chromium was applied as potassium dichromate, chromium trioxide, or chromium sulfate (75 to 225 ppm).

Many reports related iron deficiency chlorosis to high concentrations of trace metals. Hewitt (1948) found that the descending order of elements producing chlorosis in sugar beet was $Co^{2+} > Cu^{2+} > Zn^{2+} \geq CrO_4^{2-} > Ni^{2+} > Cr^{3+} > Mn^{2+} > Pb^{2+}$. Specific elements also gave toxic effects not obviously related to chlorosis. Plants growing with CrO_4^{2-} were dwarfed while those with chromium(III) appeared normal. Severity of toxicity was in the order $Ni^{2+} > Co^{2+} > Zn^{2+} > Cu^{2+} > CrO_4^{2-} > Cr^{3+} = Mn^{2+} = Pb^{2+}$. Hewitt (1953) also found that hexavalent chromium decreased the vigor of tomato, potato, oats,

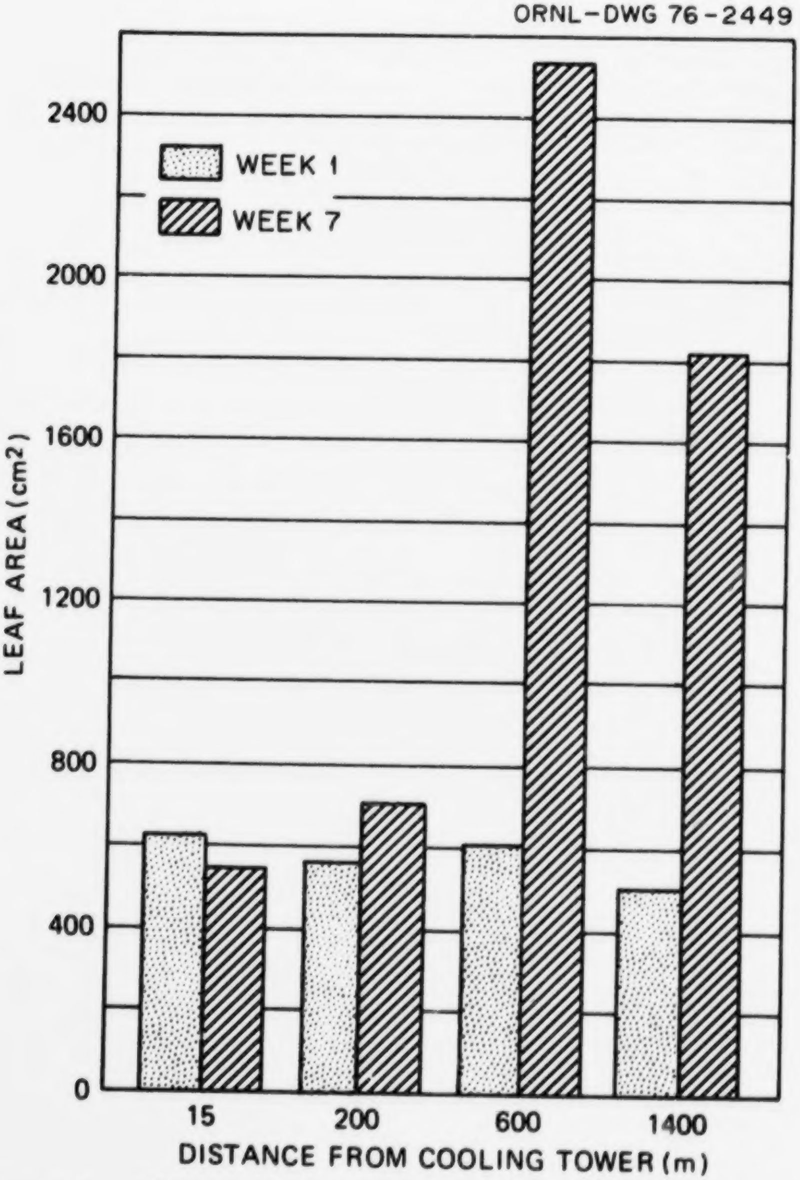

Figure 4.5. Effects of increased chromium concentrations on leaf size in tobacco exposed to cooling-tower drift. Source: Adapted from Taylor et al., 1975, Figure 6, p. 418.

and kale to a greater extent than did trivalent chromium. In sugar beet, tomato, and potato, both hexavalent and trivalent chromium produced chlorosis that could be diagnosed as iron deficiency.

DeKock (1956) investigated the effect of heavy metals in ionic or chelated form on iron chlorosis in mustard plants (*Sinapsis alba*) and observed no chlorosis with 2 ppm chromium, although yield was slightly reduced. With ionic chromium, roots appeared stunted; however, with chelated chromium no chlorosis or inhibition of root growth was observed. The order of effectiveness of the metals in producing chlorosis was Cu > Ni > Co > Zn > Cr > Mn. DeKock postulated that the metals acted in the root to prevent translocation of iron, which is necessary for chlorophyll formation to tops and thus induced chlorosis. The order of heavy metal toxicity to rice was Cd > Cu > Ti > Zn > Cr > Mo for water-filled paddies; the order in a dry field was Cd > Cu > Zn > Mo > Cr (Nagai, 1973*a*). Growth inhibition for the Kanamachi turnip decreased in the order Na > Cd > Zn > Cu > Ti > Cr > Mo (Nagai, 1973*b*).

Verfaillie (1974) reported that no abnormal physiological effects were observed in rice plants maintained in nutrient solutions supplemented with 10^{-4} M chromium(III) over a 2.5-day period or with 10^{-4} M chromium(III)-EDTA over a 5-day period. With chromium(VI) (as CrO_4^{2-}) concentrations greater than 2×10^{-5} M, some leaves and stems began to turn yellow and to wither.

Stanley (1974) found 50% inhibition of root weight of the water milfoil at 1.9 ppm $Cr_2O_7^{2-}$ and at 9.9 ppm chromium(III); 50% inhibition of shoot weight occurred at 2.6 ppm $Cr_2O_7^{2-}$ and 14.6 ppm chromium(III).

Breeze (1973) compared the toxicity of chromium(III) and chromium(VI) (as $Cr_2O_7^{2-}$) in *Lolium perenne* seedlings. Germinated seeds were exposed to solutions containing 10, 50, 100, and 500 ppm chromium for 60 hr prior to planting in soil; survival was measured a week later. At 10, 50, 100, and 500 ppm chromium(III), survivals were 84%, 63%, 35%, and 1%, respectively. Survivals for 10, 50, 100, and 500 ppm $Cr_2O_7^{2-}$ were 84%, 72%, 47%, and 2%, respectively.

Thus, chromium can be toxic to plants; the concentration at which effects are first observed depends on the species. Because chromium is not easily translocated, effects on root growth might be expected. At high chromium concentrations, inhibition and stunting of root growth as well as chlorosis and inhibition of shoot growth have been observed. There appears to be no single characteristic symptom of chromium injury (Yopp, Schmid, and Holst, 1974). The above symptoms are all gross phenotypic abnormalities which must certainly be preceded by altered metabolic patterns. However, no data on abnormal metabolism in plants exposed to low or high chromium concentrations or on the mechanisms responsible for the observed symptoms have been reported.

SECTION 4

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SECTION 5

BIOLOGICAL ASPECTS IN ANIMALS

5.1 SUMMARY

Most studies of the effects of chromium on animals have used aquatic species: fish, crustaceans, polychaete worms, and insects. Effects on birds or on wild and domestic mammals have not been reported, but some concentration data were found. The effect of chromium on mammals and chromium metabolism are discussed in Section 6.

Experimental evidence has indicated that trivalent and hexavalent chromium are the forms most significant to biological systems; both species are readily adsorbed to body surfaces. Hexavalent chromium is accumulated by marine animals, whereas the trivalent form is not. Absorption and accumulation are passive actions dependent on chromium concentration.

High chromium concentrations can produce several physiological changes in aquatic species. Growth reduction, decreases in hematocrit values and protein content, impairment of reproduction, and increased oxygen consumption have occurred in animals exposed to chromium.

Although trivalent chromium has been found to be toxic to several animals, hexavalent chromium is generally more toxic. Water properties such as pH, temperature, alkalinity, and hardness are factors influencing chromium toxicity. In addition, various animal species display different sensitivities to chromium. The lethal chromium level for invertebrates has been reported as 0.05 ppm (National Academy of Sciences and National Academy of Engineering, 1972); therefore, any water quality standards should be well below this level.

5.2 METABOLISM

5.2.1 Uptake and Absorption

Investigations of chromium uptake by animals have primarily used marine and freshwater species. In their natural environment, mollusks accumulate trace metals at various rates. Accumulation of these metals in tissues is affected by the species involved, water temperature and pH, concentration of the metal, and physiological and biochemical activity of the animal. Chromium ions are adsorbed to shells and passively taken into aquatic species through gills which act as ion exchangers. Although chromium can exist in several valence states, the trivalent and hexavalent forms are the ones important in biological systems. These forms behave differently when added to aqueous solutions. Trivalent chromium added as chromic chloride results in hydroxide formation and precipitation (Chipman, 1967); the particles formed readily adsorb to surfaces. Hexavalent chromium (sodium chromate) forms a true solution containing no particulate matter.

Baudouin and Scoppa (1974*a*) reported that accumulation of trivalent ^{51}Cr in zooplankton (*Eudiaptomus*, *Cyclops*, and *Daphnia*) occurred rapidly and that uptake increased with increasing external concentrations, which suggests that uptake is a passive process. Surface adsorption of trivalent ^{51}Cr was small; however, in organisms which do not accumulate chromium to any large extent, this adsorption may account for up to 30% of total uptake. In oxygenated natural waters with high alkaline values, chromate ions are stable. Copepods (*Eudiaptomus* and *Cyclops*) did not accumulate hexavalent ^{51}Cr, whereas *Daphnia* did so rapidly.

Chipman (1967) investigated the accumulation of ^{51}Cr by *Hermione hystrix*, a polychaete worm. The worms were placed in seawater suspensions containing either chromic chloride or sodium chromate. Worms in seawater suspensions with trivalent chromium present in the bottom silt had chromium on body surfaces and within the digestive tract. Accumulation did not occur because the trivalent form was not absorbed from the digestive tract. When *Hermione* was exposed to seawater which contained chromate, uptake of hexavalent chromium was rapid. Accumulation, which occurred slowly with no diminution, was expressed as the ratio of radioactivity per gram of live worm to that of a milliliter of seawater (Figure 5.1). Uptake of hexavalent chromium increased as the chromium concentration in seawater increased, which indicated that chromium uptake by *Hermione* was a passive process. Accumulation possibly occurred by the binding of chromium to some body proteins.

Chromium was absorbed by the polychaete worm *Nereis virens* (Raymont and Shields, 1963). In a solution containing 1 ppm chromium as sodium chromate, *Nereis* reduced the chromium concentration by amounts ranging from 0.06 to 0.1 ppm. This reduction apparently was due to chromium uptake by

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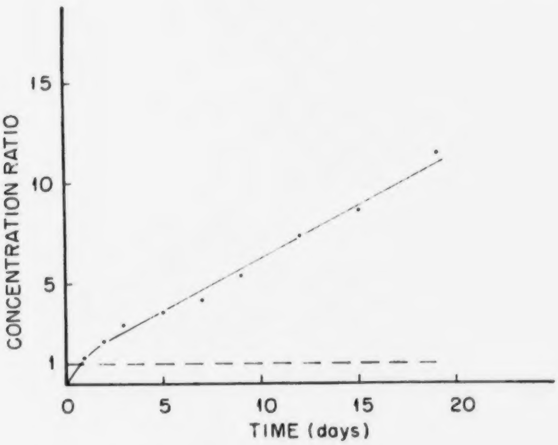

Figure 5.1. Accumulation of ^{51}Cr by *Hermione hystrix* from seawater containing the radionuclide in the form of chromate. Source: Adapted from Chipman, 1967, Figure 1, p. 935. Reprinted by permission of the publisher.

the worm. Chromium was absorbed through the gut and body walls; the parapodial region had a high chromium concentration because the body wall was thinner in this area.

Uptake of metal ions from aquatic systems by shellfish has been studied. Chipman (1966) investigated ^{51}Cr uptake by the clam, *Tapes decussatus*. Clams placed in seawater containing trivalent ^{51}Cr rapidly became radioactive from their filtering activity and adsorption of chromium particles on shells, folds of gills, mantle, and other surfaces in contact with the seawater. These particles were quickly eliminated by the clam; the body tissues did not accumulate trivalent ^{51}Cr. Trivalent chromium chelated with ethylenediaminetetraacetic acid (EDTA) was not taken up by the clam. Clams in contact with seawater containing hexavalent chromium rapidly took up the chromium ions by adsorption and accumulated a small amount of chromium in the tissues. Amounts of chromium entering the clam were related to the chromium concentration in the seawater, which indicated that uptake was a passive process. These results corroborated Chipman's earlier investigations of chromium uptake by *Hermione* sp.

Chromium was found in shells of the oyster *Crassostrea virginica* in higher concentrations than in the seawater from which the oysters were taken (Ferrell, Carville, and Martinez, 1973). Since chromium can form carbonates, the oyster possibly incorporated chromium as the shell formed. Soft tissues of the oyster *Crassostrea gigas* were analyzed for uptake of various metals (Ayling, 1974). The concentration of chromium in the oyster was independent of the concentration in the water. In contrast to previous reports, this study suggested that chromium had been absorbed by some physiological process up to a maximum concentration that depended on oyster size.

Physiological movement of chromium has also been studied in the crab *Cancer magister* (Tennant and Forster, 1969). Chromium was found in the gills, setae, and hepatopancreas. Since chromium is adsorbed on surfaces, it is associated with organs having a high surface-area to volume ratio. The setae and gills have this high ratio, which suggests that chromium was adsorbed to their surfaces. However, chromium present in the hepatopancreas must have been ingested and/or diffused across gill membranes. The authors suggested that a metabolic movement of chromium was involved, which indicated a physiological process in chromium uptake. Chromium was taken up in greatest concentration by the gills of the crab *Podophthalmus vigil* exposed to 1 µCi ^{51}Cr per liter (Sather, 1967). Sather proposed that ^{51}Cr was bound to proteins and possibly to mucopolysaccharides.

A study using rainbow trout, *Salmo gairdneri*, showed that chromium uptake was passive (Fromm and Stokes, 1962). Uptake occurred with fish exposed to 0.0013 and 0.0100 ppm chromium as potassium chromate. The amount of chromium accumulated was proportional to the amount of chromium present in the water and leveled off after 10 days of exposure. Each point on Figure 5.2 represents the mean value for four fish. Broken lines show the mean maximum uptake and solid lines are regression lines for uptake. At chromium concentrations of 0.01 and 0.0013 ppm in water, the mean maximum chromium concentrations in the trout were 133.6 and 16.6 ppm, respectively. Rainbow trout exposed to 18.6 ppm chromium had a total chromium uptake by the liver, ORNL DWG 76-2451

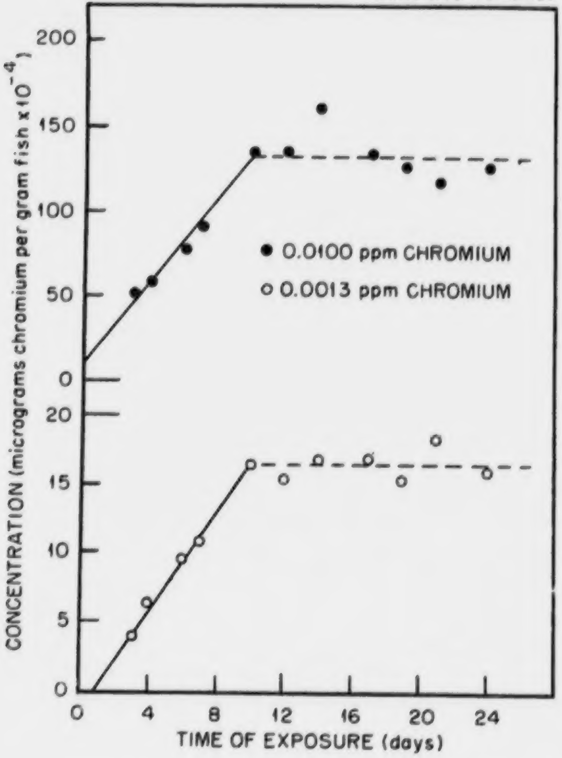

Figure 5.2. Uptake of hexavalent chromium by two groups of rainbow trout exposed to 0.0100 and 0.0013 ppm chromium. Source: Fromm and Stokes, 1962, Figure 1, p. 1152. Reprinted by permission of the publisher.

spleen, kidney, and gall bladder of 72.5 μg per fish during a 24-hr exposure (Schiffman and Fromm, 1959).

5.2.2 Transport and Distribution

Table 5.1 gives the chromium distribution in tissues of some wild and domestic mammals; Table 5.2 lists chromium content of hair in various animal species. Chromium distribution in some aquatic species is summarized in Table 5.3.

Elemental analyses of tissues of cotton rats chronically subjected to ingestion and inhalation pathways (cooling-tower drift) have been compared to those of animals remote from exposure (Table 5.4) (Taylor, 1975). Significant differences ($P < 0.01$) in chromium concentrations in pelt, hair, and bone were identified between exposed and control animals. Chromium concentrations in bones of exposed and control animals ranged from 0.46 to 0.16 ppm, whereas concentrations in hair and pelt of animals exposed to drift ranged from 4.4 to 1.1 ppm, respectively. These elevated levels in exposed animals were contrasted to 0.4 and 0.1 ppm in hair and pelt of control

Table 5.1. Chromium in wild and domestic animal tissues

Tissue	Wild animals		Domestic animals	
	Number of samples	Chromium concentration (ppm wet wt)	Number of samples	Chromium concentration (ppm wet wt)
Liver	9	0.16	16	0.15
Kidney	12	0.20	7	0.16
Heart	11	0.14	11	0.0
Lung	3	0.24		
Spleen	5	0.48		
Muscle	4	0.11		
Stomach	1	0.04		
Placenta	1	0.07		

Source: Adapted from Schroeder, 1970, Table 5, p. 9. Reprinted by permission of the publisher.

animals. With the exception of the gastrointestinal tract, chromium was evenly distributed among organs of control animals. Little evidence of bioaccumulation was found among animals exposed to elevated levels of chromium.

Huckabee, Cartan, and Kennington (1972) analyzed the hair of several mammals from Idaho and Wyoming for concentrations of trace metals, including chromium (Table 5.2). Chromium was found in 61% of the samples; levels varied widely among members of the same species from the same geographic area as well as among different species.

Trivalent chromium concentrations in *Hermione* were 10,373, 5,410, and 3,713 counts min^{-1} g^{-1} at 9, 15, and 22 days of exposure, respectively (Chipman, 1967). Trivalent chromium was not concentrated to any large extent; concentration factors were 0.59 at 9 days, 0.31 at 15 days, and 0.21 at 22 days. Hexavalent chromium concentrations ranged from 0.4 mg/g (live wt) at 1 day of exposure (0.3 ppb added as sodium chromate) to 3.6 mg/g (live wt) at 19 days of exposure. The concentration factor was approximately 10 at 19 days.

Other studies showed that chromium was absorbed by *Nereis* in several areas of the body (Raymont and Shields, 1963). The blood vessels had high chromium concentrations. Chromium was transported from the body and gut walls to small blood vessels in these regions. A chromium gradient was

Table 5.2. Chromium concentrations in the hair of several wild animal species

Species	Location	Chromium concentration in sample (ppm)
Antilocapra americana (pronghorn antelope)	Lemhi Range, Idaho	44
	Lemhi Range, Idaho	120
	Lemhi Range, Idaho	18
	Lemhi Range, Idaho	36
	Lemhi Range, Idaho	110
	Lemhi Range, Idaho	4.7
	Lemhi Range, Idaho	6.6
	Lemhi Range, Idaho	160
	Lemhi Range, Idaho	480
	Lemhi Range, Idaho	1.9
	Lemhi Range, Idaho	98
	Lemhi Range, Idaho	640
	Lemhi Range, Idaho	370
	Lemhi Range, Idaho	120
	Lemhi Range, Idaho	6.8
	Lemhi Range, Idaho	Trace
	Lemhi Range, Idaho	440
	Lemhi Range, Idaho	55
	Laramie Basin, Wyo.	130
	Laramie Basin, Wyo.	9.9
	Wamsutter Area, Wyo.	2.8
	Wamsutter Area, Wyo.	0.3
	Shirley Basin, Wyo.	30
	Shirley Basin, Wyo.	6.7
	Shirley Basin, Wyo.	9.0
Odocoileus hemionus (mule deer)	Lemhi Range, Lost River Mts., Idaho	13
	Lemhi Range, Lost River Mts., Idaho	22
	Lemhi Range, Lost River Mts., Idaho	48
	Lemhi Range, Lost River Mts., Idaho	57
	Lemhi Range, Lost River Mts., Idaho	310
	Lemhi Range, Lost River Mts., Idaho	51
	Lemhi Range, Lost River Mts., Idaho	92
	Lemhi Range, Lost River Mts., Idaho	420
	Lemhi Range, Lost River Mts., Idaho	630
Cervus canadensis (elk)	Soldier Mts., Idaho	570
	Soldier Mts., Idaho	83
	Soldier Mts., Idaho	240
	Soldier Mts., Idaho	9
	Soldier Mts., Idaho	84
	Soldier Mts., Idaho	57
	Soldier Mts., Idaho	16
	Soldier Mts., Idaho	1.9
	Soldier Mts., Idaho	13
	Soldier Mts., Idaho	13
Oreamnos americanus (mountain goat)	Lemhi Range, Idaho	4.0
	Lemhi Range, Idaho	5.5
Sorex vagrans (shrew)	Jackson Hole, Wyo.	15
Microtus pennsylvanicus (meadow vole)	Jackson Hole, Wyo.	5.6
	Jackson Hole, Wyo.	8.8
	Gros Ventre Range, Wyo.	8.2
Microtus montanus (mountain vole)	Jackson Hole, Wyo.	16
	Jackson Hole, Wyo.	180
	Jackson Hole, Wyo.	85

Table 5.2 (continued)

Species	Location	Chromium concentration in sample (ppm)
Microtus montanus (mountain vole)	Jackson Hole, Wyo.	160
	Jackson Hole, Wyo.	21
	Jackson Hole, Wyo.	150
	Jackson Hole, Wyo.	23
	Jackson Hole, Wyo.	82
	Jackson Hole, Wyo.	44
	Jackson Hole, Wyo.	9.9
	Jackson Hole, Wyo.	30
	Jackson Hole, Wyo.	58
	Jackson Hole, Wyo.	49
	Jackson Hole, Wyo.	21
	Gros Ventre Range, Wyo.	4.7
Zapus princeps (western jumping mouse)	Jackson Hole, Wyo.	45
	Jackson Hole, Wyo.	24
	White Cloud Peaks, Idaho	0.7
	White Cloud Peaks, Idaho	4.3
Erethizon dorsatum (rodent)	Gros Ventre Range, Wyo.	0.9
	Gros Ventre Range, Wyo.	0.8
Eutamis sp. (rodent)	Gros Ventre Range, Wyo.	29.1
Microtus richardsoni (rodent)	Gros Ventre Range, Wyo.	10
Microtus longicandus (rodent)	White Cloud Peaks, Idaho	0.7
	White Cloud Peaks, Idaho	4.3
	White Cloud Peaks, Idaho	1.7
Canis latrans (coyote)	Jackson Hole, Wyo.	5.8
	Jackson Hole, Wyo.	1.6
	Jackson Hole, Wyo.	1.5
	Jackson Hole, Wyo.	12
	Jackson Hole, Wyo.	0.9
	Jackson Hole, Wyo.	5.3
	Jackson Hole, Wyo.	4.8
	Jackson Hole, Wyo.	0.6
	Jackson Hole, Wyo.	4.2
	Jackson Hole, Wyo.	3.5
	Jackson Hole, Wyo.	0.7
	Jackson Hole, Wyo.	2.0
	Jackson Hole, Wyo.	6.2
	Jackson Hole, Wyo.	2.1
	Jackson Hole, Wyo.	3.3

Source: Compiled from Huckabee, Cartan, and Kennington, 1972.

found across the gut wall into the blood vessels. Actual chromium concentrations in tissues were not reported. Chromium concentrations in limpets (*Patella vulgata*) collected near a sewage outfall ranged from 9.7 to 23.2 ppm in the soft tissues and from 9.3 to 10.4 ppm in skeletal parts (Navrot, Amiel, and Kronfeld, 1974).

In the clam, *Tapes decussatus*, chromium was distributed throughout the absorptive surfaces of the body (Chipman, 1967). Most trivalent ^{51}Cr was found in shells, folds of gills, and the mantle. The concentration ratio was <1.0. Hexavalent ^{51}Cr was found primarily in soft tissues, with only a small percentage in shells. At 20 days of exposure, the concentration factor was 12 to 16. Chromium concentrations in clam shells and meats are given in Table 5.5.

Table 5.3. Accumulation of chromium in various tissues of aquatic organisms

Species	Chromium concentration in seawater	Tissue or organ	Chromium concentration in tissue	Concentration factor
Crassius auratus	10-13.0 μCi injected into air bladder	Intestine	25 counts min^{-1} mg^{-1}	
		Liver	25-40 counts min^{-1} mg^{-1}	
		Pancreas	25-40 counts min^{-1} mg^{-1}	
		Spleen	60-100 counts min^{-1} mg^{-1}	
		Kidney	200 counts min^{-1} mg^{-1}	
		Head kidney	275 counts min^{-1} mg^{-1}	
		Gill	40-60 counts min^{-1} mg^{-1}	
		Muscle	10 counts min^{-1} mg^{-1}	
		Backbone	30-40 counts min^{-1} mg^{-1}	
		Gonad	30-60 counts min^{-1} mg^{-1}	
		Air bladder	1,000 counts min^{-1} mg^{-1}	
Lampsilis radiata	0.204 pCi/ml	Soft tissues	89.6 pCi/g	440
Hermione (whole)	17,804 counts min^{-1} g^{-1}		10,373 counts min^{-1} g^{-1} (9 days)	0.59
	17,833 counts min^{-1} g^{-1}		5,410 counts min^{-1} g^{-1} (11 days)	0.31
	18,226 counts min^{-1} g^{-1}		3,713 counts min^{-1} g^{-1} (22 days)	0.21
	0.31 ppb			3.0 (5 days)
				3.5 (7.5 days)
				5.0 (9.0 days)
				7.5 (12.5 days)
				8.0 (15.0 days)
				12.0 (19.0 days)
	0.1 ppb		8.1 ppm (1 day, dry)	
	0.3 ppb		0.4 ppm (2 days, live)	
	0.3 ppb		0.7 ppm (3 days, live)	
	0.3 ppb		0.9 ppm (5 days, live)	
	0.3 ppb		1.1 ppm (7 days, live)	
	0.3 ppb		1.3 ppm (9 days, live)	
	0.3 ppb		1.7 ppm (12 days, live)	
	0.3 ppb		2.3 ppm (15 days, live)	
	0.3 ppb		2.7 ppm (19 days, live)	
	3.0 ppb		14.0 ppm (4 days, live)	
	3.0 ppb		22.0 ppm (8 days, live)	
	3.0 ppb		26.0 ppm (11 days, live)	
	3.0 ppb		34.0 ppm (15 days, live)	
	10 ppb		24 ppm (2 days)	
	10 ppb		40 ppm (4 days)	
	10 ppb		53 ppm (8 days)	
	10 ppb		68 ppm (11 days)	

Table 5.3 (continued)

Species	Chromium concentration in seawater	Tissue or organ	Chromium concentration in tissue	Concentration factor
	10 ppb		84 ppm (11 days)	
	10 ppb		108 ppm (13 days)	
	100 ppb		206 ppm (3 days)	
	100 ppb		288 ppm (6 days)	
	100 ppb		428 ppm (11 days)	
	100 ppb		495 ppm (14 days)	
	500 ppb		856 ppm (3 days)	
	500 ppb		1139 ppm (6 days)	
	500 ppb		1436 ppm (11 days)	
	500 ppb		1834 ppm (14 days)	
Mummichog	1 = concentration of phytoplankton culture – chromium transferred down food chain	Gonad		9.0
		Muscle		0.5
		Gills		1.7
		Spleen		6.9
		Liver		1.7
		Digestive tract		2.2
Zooplankton, postlarvae fish (whole)	132 MCi/mg = initial concentration in phytoplankton culture			9.9
				7.3
				6.2
Podophthalmus vigil	1 µCi $CrCl_3$ per liter	Gills	5000 dis min^{-1} mg^{-1} (max, 2 days)	
	1 µCi $CrCl_3$ per liter	Muscle	79-80 dis min^{-1} mg^{-1} (max, 2-4 days)	
	1 µCi $CrCl_3$ per liter	Midgut gland	75 dis min^{-1} mg^{-1} (max, 6 days)	
	1 µCi $CrCl_3$ per liter	Carapace	50 dis min^{-1} mg^{-1} (max, 14 days)	
	1 µCi $CrCl_3$ per liter	Blood	10 dis min^{-1} mg^{-1} (max, 16 days)	

Source: Adapted from National Academy of Sciences and National Academy of Engineering, 1972, Table 3, pp. 469-480. Data collected from various sources.

Table 5.4. Comparison of chromium distribution pattern in cotton rats (*Sigmodon hispidus*) exposed to cooling-tower drift and in control animals

Organ or tissue	Number of animals		Chromium concentration (ppm ± 1 SE)	
	Control	ORGDP[a]	Control	ORGDP[a]
Heart	6	6[b]	0.105 ± 0.013	0.124 ± 0.016
Liver	6	6[b]	0.046 ± 0.016	0.160 ± 0.039
Kidney	6	6[b]	0.087 ± 0.014	0.124 ± 0.040
Spleen	6	6[b]	0.493 ± 0.123	0.713 ± 0.084
Lung	6	6[b]	0.289 ± 0.072	0.292 ± 0.063
Bone	6	6[b]	0.160 ± 0.008	0.460 ± 0.024[c]
Muscle	6	6[b]	0.234 ± 0.043	0.288 ± 0.029
Gastrointestinal tract	6	6[b]	1.046 ± 0.277	1.006 ± 0.183
Pelt	6	24	0.092 ± 0.007	1.056 ± 0.133[c]
Hair	6	24	0.395 ± 0.021	4.397 ± 0.555[c]
Residual[d]	6	24	0.200 ± 0.032	0.311 ± 0.025

[a] ORGDP = Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee.
[b] Six pooled samples of four animals each.
[c] $p < 0.01$ significant difference.
[d] Blood, reproductive organs, brain, salivary glands, and thyroid.

Source: Adapted from Taylor, 1975, Table 6, p. 4.

Table 5.5. Uptake of chromate by *Tapes decussatus* exposed to different chromium concentrations in seawater

Exposure (days)	Chromium uptake at the seawater concentrations indicated (ppb)[a]		
	3 ppb	10 ppb	100 ppb
		Shells	
5	7.0	5.1	5.0
10	15.5	13.6	9.8
15	21.5	18.0	16.0
20	27.3	26.0	18.0
		Meats	
5	37.4	55.8	775
10	44.2	129.4	1879
15	80.7	231.8	2750
20	84.0	275.1	2470

[a] Calculated from the specific activities of ^{51}Cr.

Source: Adapted from Chipman, 1966, Table II, p. 579. Reprinted by permission of the publisher.

Harvey (1969) found the ^{51}Cr concentration in soft tissues of freshwater clams exposed to 0.204 pCi/ml was 89.6 pCi/g, with a concentration factor of 440. Oyster shells from various parts of the United States were analyzed for heavy-metal concentrations (Ferrell, Carville, and Martinez, 1973). Chromium concentrations, which ranged from 0.05 to 7.26 ppm, were considerably higher in shells than in seawater and represented at least a thousandfold increase. Ayling (1974) found that the Pacific oyster, *Crassostrea gigas*, contained 1 to 37 ppm chromium (dry wt) in soft tissues. Mud samples from beds inhabited by these oysters contained 2 to 88 ppm chromium; thus, a very small concentration factor for oysters was indicated. Ayling noted that care must be taken in interpreting concentration factors since values based on seawater and mud vary widely. In a survey of various mollusks, Pringle et al. (1968) reported chromium concentrations of 0.04 to 3.40 ppm (wet wt) for U.S. East Coast oysters, 0.1 to 0.3 ppm (wet wt) for U.S. West Coast oysters, 0.1 to 5 ppm (wet wt) for soft shell clam, and 0.19 to 5.80 ppm (wet wt) for northern quahaug.

Sather (1967) found that the gills of crabs probably regulated the amount of chromium absorbed by blood. Chromium passed through the gills and was transported by the blood to other tissues. Intrapericardial injection of radiochromium resulted in loss of ^{51}Cr from the blood to the gills, where it was internally bound. Muscle tissues had greater affinity for chromium than other tissues and thus reached equilibrium shortly after the gills. Chromium concentrations in various organs are shown in Figure 5.3.

Several studies concerning chromium concentrations in fish have been conducted. Tong et al. (1974) reported that the chromium concentration in lake trout (*Salvelinus namaycush*) from Lake Cayuga in New York generally increased with trout age. At 1 year of age, chromium content was 5.2 ppb (fresh wt); at 12 years, the chromium concentration was 90 ppb (fresh wt). Several species of fish from the Great Lakes were analyzed for trace elements (Lucus, Edgington, and Colby, 1970). Chromium concentrations (micrograms per gram of tissue) in whole fish were: Lake Michigan alewife, 1.1 ± 0.5; Lake Michigan spottail shiner, 0.9 ± 0.5; Lake Erie spottail shiner, 10; Lake Michigan trout-perch, 1.6 ± 0.2; and Lake Superior trout-perch, ≤ 3. Uthe and Bligh (1971) surveyed several fish species from Canadian lakes. The chromium concentrations of dressed fish in parts per million wet weight were: lake whitefish (Moose Lake), 0.033; lake whitefish (Lake Ontario), <0.017; northern pike (Moose Lake), <0.035; northern pike (Lake St. Pierre), <0.026; northern pike (Lake Erie), <0.031; rainbow smelt (Lake Erie), 0.034; and yellow perch (Lake Erie), <0.065.

Again, it is necessary to add a note of caution about the analytical uncertainty of numbers such as those given above. All values must be regarded as tentative until the methods of analyses for traces of chromium are better understood. Comparison of numbers from different laboratories or different methods is particularly hazardous.

5.2.3 Elimination

Marine polychaete worms have been used to investigate the retention and rate of loss of ^{51}Cr. *Hermione* sp. exposed 12 days to seawater with

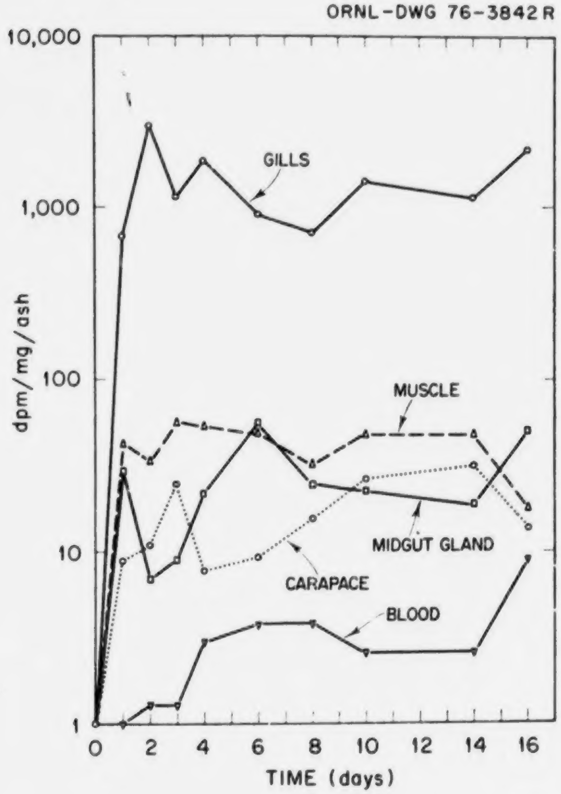

Figure 5.3. Accumulation from solution of ^{51}Cr by the crab, *P. vigil*. Source: Sather, 1967, Figure 1, p. 951. Reprinted by permission of the publisher.

chromate added showed more than one rate of loss (Chipman, 1967). The biological half-life was 123 days for the long-lived component and 7.95 days for the short-lived component (Figure 5.4). In *Hermione*, chromium seemed to be present in two components with a different type of binding in each. The slow turnover rate indicated a component that was bound differently. The long, steady rate of accumulation indicated that the larger part of ^{51}Cr accumulated from long-term exposure was bound in a body component having a slow turnover rate.

In a retention study using the freshwater clam, *Lampallis radiata*, the biological half-life of ^{51}Cr also had both short- and long-lived components (Harvey, 1969). The half-life of the short-lived component was 5 days and that of the long-lived component was 52 days. In comparison with the marine worm *Hermione*, ^{51}Cr has a shorter biological half-life in clams than in marine worms.

Studies by Sather (1967) indicated that the gills of crabs exposed to ^{51}Cr lost chromium at a daily rate of 263 dis min^{-1} mg^{-1} when the gills were placed in water without chromium. The biological half-life was nine to ten

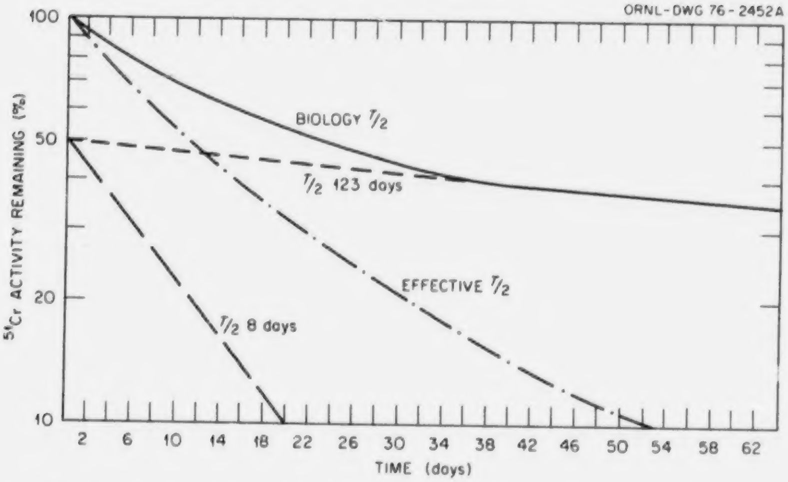

Figure 5.4. Retention of ^{51}Cr by *Hermione hystrix* following a 12-day exposure to the radionuclide in high specific activity in seawater in the form of chromate. Source: Adapted from Chipman, 1967, Figure 2, p. 938. Reprinted by permission of the publisher.

days. Chromium loss was attributed to mobilization of chromium by the blood and its deposition in other tissues.

Brown crickets were fed radiolabeled chromium (as chromium chloride), were transferred to nonradioactive food, and then their whole-body retention was measured (Van Hook and Crossley, 1969). The retention of ^{51}Cr was described in a two-component model. From a single ingestion, an estimated 95% of the initial body burden was eliminated within 48 hr with a biological half-time of 4 hr. Less than 6% of the nuclide ingested was actually assimilated by the tissues. The assimilated fraction (short-time component) was eliminated at a slower rate with a biological half-time of 83 hr. The low assimilation and moderate excretion rates indicate that the ^{51}Cr concentration would probably be reduced at each trophic transfer.

The significance of chronic exposure to chromium by ingestion was determined in retention studies of native mammals (Taylor, 1975). Elimination of ^{51}Cr (as $Na_2{}^{51}CrO_4$) by cotton rats resulted in a two-component curve — a short component representing gut clearance and a long component illustrating loss of the assimilated fraction. The percent assimilated was 0.8% of the initial whole-body radioactivity. Within three days after feeding, 99% was eliminated (Figure 5.5), whereas the remaining fraction (<1%), which represented loss of the assimilated radionuclide, was eliminated at a slower rate. The biological half-time of the assimilated chromium was calculated to be 693 days. These data confirm the lack of any bioaccumulation from contaminated food as depicted in stable analyses (Table 5.4) and suggest the reduced probability of a toxic effect due to the low assimilation and rapid excretion rates.

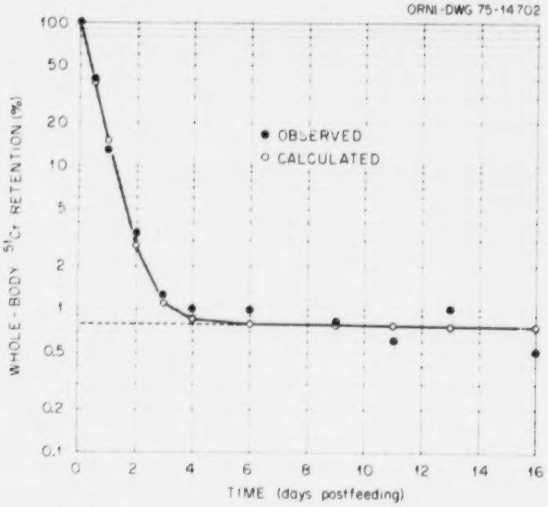

Figure 5.5. Retention of ^{51}Cr by *Sigmodon hispidus*. Source: Adapted from Taylor, 1975, Figure 1.

5.3 EFFECTS

5.3.1 Physiological Effects

Biesinger and Christensen (1972) reported the effects of several metals on the metabolism of *Daphnia magna*. Animals exposed to 0.619 ppm trivalent chromium (added as chromic chloride) in Lake Superior water (pH 7.4) had a weight reduction of 11% when compared with control animals. The amount of total protein per animal was reduced by 3%. The effect of chromium on metabolism was measured by glutamic oxalacetic transaminase (GOT) activity. The GOT activity per animal exposed to 0.619 ppm chromium was reduced by 4% when compared with controls. Reproduction was also affected; a chromium concentration of 0.33 ppm resulted in a 16% reproduction impairment. When *Daphnia pulex* was exposed to sodium dichromate, a hexavalent chromium compound, oxygen consumption was altered (Sherr and Armitage, 1973). The oxygen consumption per animal was approximately doubled in the group exposed to 0.01 ppm dichromate (temperature 21°C) as compared with the control group.

Fromm (1970) studied the effects of chronic chromium exposure on rainbow trout, *Salmo gairdneri*. Fish exposed to 0.2 ppm chromium for one week had plasma cortisol levels almost double that of controls (0.54 μg/ml for exposed fish, 0.27 μg/ml for controls). After exposure for two and three weeks, exposed fish had plasma levels similar to those of controls. Effects of chromium on the blood of *S. gairdneri* were also reported by Schiffman and Fromm (1959). Trout exposed to 20 ppm chromium showed a significant increase in red blood cells. Both splenectomized and intact fish exposed to 20 ppm chromium had hematocrits significantly higher than controls. Blood of splenectomized fish exposed to chromium also had a significantly higher hemoglobin content than did the blood from nonexposed splenectomized fish. The chromium-exposed intact fish had larger blood cells than did the controls. These effects are summarized in Table 5.6. The authors suggested that the increase in hematocrits resulted from decreased plasma volume and increased cell number and cell size. A chromium concentration of 2 to 4 ppm affected the hematocrit.

5.3.2 Toxicity

Because heavy-metal salts in solution are stable compounds, they constitute a serious form of pollution. Chromium toxicity to aquatic organisms has been shown to vary with solution pH, water hardness, temperature, species, size of organism, and the chemical form of chromium. A few studies have reported trivalent chromium to be only slightly toxic to several organisms. In soft water, trivalent chromium appears to be the form most lethal to fish, whereas in hard water, hexavalent chromium has the greatest toxicity. In hard water, the toxicity of trivalent chromium is reduced by the formation of precipitates; hexavalent chromium remains toxic under these conditions. The susceptibility of organisms to trivalent chromium is complicated by the acidity of most trivalent chromium salts.

Fish appear to be more tolerant of chromium salts than lower forms of aquatic organisms. Exposure to low chromium concentrations over a long period produces a more detrimental effect on the organism than does a high-dose exposure for a brief period. Toxic effects to aquatic organisms are summarized in Tables 5.7 and 5.8.

Studies of chromium toxicity in mammals have been concerned primarily with experimental animals (rats, mice, and guinea pigs) and man and thus will be discussed in Section 6.

Nereis sp. showed sensitivity to hexavalent chromium salts (Raymont and Shields, 1963). Responses to sodium and potassium chromates and dichromates did not differ. Chromium concentrations of 2 to 10 ppm produced heavy mortality in two to three weeks. The threshold toxicity level for *Nereis* was just under 1 ppm chromium.

Several studies concerning the effects of chromium on *Daphnia* sp. have been reported. For example, chromium was added to Lake Erie water in the form of chromic chloride to determine its effects on *Daphnia magna* (Anderson, 1948). The approximate 50% lethal concentration (LC_{50}) for chromic chloride was <3.6 ppm (0.000023 *M*). At this concentration the solution became acid and a precipitate formed. This precipitate may have been responsible for immobilizing the daphnids either by mechanical means or by a specific toxic action. Daphnids were found to be particularly susceptible during molting. After three weeks, the LC_{50} reported for *Daphnia magna* by Biesinger and Christensen (1972) was 2.0 ppm chromium in Lake Superior water. For Lake Erie water, the 64-hr approximated threshold was <1.2 ppm. These results tend to substantiate the work of Anderson (1948).

The survival of *Daphnia pulex* exposed to various concentrations of sodium dichromate showed that *Daphnia* displayed no adverse reaction to low

Table 5.6. The effect of exposure to 20 ppm chromium on the blood of rainbow trout, *Salmo gairdneri*[a]

Treatment	Hematocrit (ml/100 ml)	Hemoglobin (g/100 ml)	Red blood cells count (million mm^3)	Red blood cells length (μ)	Plasma volume (ml/100 g)	Blood volume (ml/100 g)
Intact trout						
Clean tap water	31.8 ± 1.39	6.5 ± 1.27	1.11 ± 0.098	14.69 ± 0.24	2.13 ± 0.14	3.24 ± 0.16
Chromium water[b]	43.8 ± 1.56	6.6 ± 0.25	1.25 ± 0.032	14.93 ± 0.15	1.61 ± 0.12	3.01 ± 0.18
Splenectomized trout						
Clean tap water	28.5 ± 1.42	5.6 ± 1.13	1.04 ± 0.18		2.44 ± 0.12	3.85 ± 0.16
Chromium water[b]	40.6 ± 2.92	7.4 ± 0.51	1.38 ± 0.11		1.74 ± 0.10	3.16 ± 0.14

[a] All values are given as mean and standard error.

[b] Concentration of 20 ppm.

Source: Adapted from Schiffman and Fromm, 1959, Table I, p. 207. Reprinted by permission of the publisher.

Table 5.7. Toxicity of chromium to aquatic biota

Chemical compound	Test organism	Test conditions[a]	Chromium concentration (ppm)	Remarks
Ammonium chromate	*Gambusia affinis*	SB, FW, LS	270.0	48-hr TL_m (median tolerance limit), acute; turbid water
	Gambusia affinis	SB, FW, LS	212.0	48-hr TL_m, acute; turbid water
Chromic chloride	*Daphnia magna*	SB, FW, LS	<<3.6	Threshold concentration, dose just immobilizing in 64 hr; Lake Erie water
Chromic sulfate	*Daphnia magna* (cladocera)	SB, FW, LS	0.1	24-hr TL_m, acute
	Daphnia magna (cladocera)	SB, FW, LS	0.03	48-hr TL_m, acute (standard reference water)
Chromic sulfate and sodium dichromate	*Lymnaea* sp. (snail)	SB, FW, LS	0.17	24-hr TL_m, acute (standard reference water)
Chromium	*Daphnia magna* (cladocera)	SB, FW, LS	2.0	3-week TL_m, chronic; 18°C
	Daphnia magna	SB, FW, LS	0.6	50% reproduction loss in 3 weeks
	Daphnia magna	SB, FW, LS	0.33	16% reproduction loss in 3 weeks
	Gasterosteus aculeatus	SB, FW, LS	1.0	Toxic limit, acute
	Salmo gairdneri	FW, FS	20.0	No toxic effect noted
	Salmo gairdneri		31.0	No kill in 96 hr
	Cricotopus bicinctus (midgefly)	FW, FS (river)	<25	Survived and matured; resistant species
	Lepomis macrochirus	FW	170	96-hr TL_m; chromate
	Lepomis macrochirus	FW	110	96-hr TL_m; dichromate
Chromium (chromate)	*Lepomis macrochirus*	SB, FW, LS	170.0	
	Salmo gairdneri	SB, FW, LS	5.0	40% kill, 15 days
	Salmo gairdneri	SB, FW, LS	10.0–12.5	80% kill, 15 days (tissue accumulation study)
Chromium (dichromate)	*Lepomis macrochirus*	SB, FW, LS	48.4	96 hr, 100% survival
	Lepomis macrochirus	SB, FW, LS	113.0	96-hr TL_m, acute
	Lepomis macrochirus	SB, FW, LS	176.8	96 hr, 100% kill
Chromium (hexavalent)	*Lepomis macrochirus*	FW	0.2	96-hr TL_m continuous exposure
	Lepomis macrochirus			
	Lepomis macrochirus	SB, FW, LS	<50	Can survive 30 days
	Lepomis macrochirus	SB, FW, LS	<70	Can survive at least 7 days (hard water, pH 7.7–8.2)

Table 5.7 (continued)

Chemical compound	Test organism	Test conditions[a]	Chromium concentration (ppm)	Remarks
Chromium (hexavalent)	*Lepomis macrochirus*	SB, FW, LS	110.0	96-hr TL_m, acute, soft water, alkalinity and hardness reduced toxicity
	Salmo gairdneri	SB, FW, LS	2.5	Tissue accumulation-elimination study, 2.5-ppm exposure level up to 24 days
	Young salmon		<10.0	Minimum lethal concentration, freswater
	Young salmon		<17.8	Minimum lethal concentration, seawater
Chromium (trivalent)	Young salmon		50.0	Minimum lethal concentration, freshwater
	Young salmon		>50.0	Minimum lethal concentration, seawater
Chromium diboride	*Oncorhynchus kisutch*	SB, FW, LS	10.0	No kill in 24 hr; 10.0°C
	O. tshawytscha	SB, FW, LS	10.0	No kill in 24 hr; 10.0°C
	Ptychocheilus oregonensis	SB, FW, LS	10.0	No kill in 24 hr; 10.0°C
Chromium potassium sulfate	*Pimephales promelas*	SB, FW, LS	5.07 (S)[b] 6.74 (H)	96-hr TL_m, acute, in hard and soft water
	Lepomis macrochirus	SB, FW, LS	7.46 (S)	
	Lepomis macrochirus	SB, FW, LS	71.9 (H)	
	Carassius auratus	SB, FW, LS	4.10 (S)	
	Lebistes reticulatus	SB, FW, LS	3.33 (S)	
Chromium sulfate	*Anthocidaris* sp. (sea urchin)	SW, LS	3.2	No effect on development of eggs; 27°C
	Anthocidaris sp.	SW, LS	10.0	Effect on development of eggs; 27°C
	Hemicentrotus sp. (sea urchin)	SW, LS	10.0	Effect on development of eggs; 11-16°C
	Mytilus sp. (mussel)	SW, LS	3.2	No effect on development of embryos; 13-17°C
	Mytilus sp.	SW, LS	10.0	Effect on development of embryos; 13-17°C
Chromium sulfate ($6H_2O$)	Fish	FW, LS	170-200	Minimum lethal dose; distilled water, 21°C
Chromium sulfate	Fish	FW, LS	130-160	Minimum lethal dose; distilled water, 21°C
	Gasterosteus aculeatus	SB, FW, LS	5.0	Survived 24 hr; pH 6.0, 15-18°C
	Gasterosteus aculeatus	SB, FW, LS	2.0	Survived 48 hr
	Gasterosteus aculeatus	SB, FW, LS	1.2	Lethal concentration limit
Chromium sulfate (trivalent)	*Oncorhynchus kisutch*	CB, FW, LS	50.0	100% kill in 3 days
	Oncorhynchus kisutch	CB, FW, LS	>50.0	Critical level

Table 5.7 (continued)

Chemical compound	Test organism	Test conditions[a]	Chromium concentration (ppm)	Remarks
Potassium chromate	*Anthocidaris* sp.	SW, LS	3.2	No effect on development of eggs; 27°C and 15-16°C
	Hemicentrotus sp. (sea urchins)		10.0	Effect on development of eggs; 27°C and 11-16°C
	Mytilus sp. (mussel)		3.2	No effect on development of embryos; 13-17 and 27°C
	Crassotrea gigas (oyster)		10.0	Effect on development of embryos; 13-17 and 27°C
	Gambusia affinis	SB, FW, LS	722	24-hr TL_m, acute; (all data, turbid water, 17-21°C)
	Gambusia affinis	SB, FW, LS	480	48-hr TL_m, acute
	Gambusia affinis	SB, FW, LS	400	96-hr TL_m, acute
	Lepomis macrochirus	CB, FW, LS	450	96-hr TL_m, acute; small fish, 20°C
	Lepomis macrochirus	CB, FW, LS	630	96-hr TL_m, acute; medium fish, 20°C
	Lepomis macrochirus	CB, FW, LS	550	96-hr TL_m, acute; large fish, 20°C
	Lepomis macrochirus	SB, FW, LS	∿620.0	96-hr TL_m, acute, soft water; alkalinity and hardness reduced toxicity
	Pimephales promelas	SB, FW, LS	109	24-hr TL_m, acute
	Pimephales promelas	SB, FW, LS	60.4	48-hr TL_m, acute
	Pimephales promelas	SB, FW, LS	45.6	96-hr TL_m, acute (soft water)
	Salmo gairdneri	SB, FW, LS	100	24-hr TL_m, acute
	Salmo gairdneri	SB, FW, LS	20	Increased hepatocrit values from 31.8 to 43.8
	Salmo gairdneri	SB, FW, LS	1000	79 min, mean equilibrium loss; 18°C
	Salmo gairdneri	SB, FW, LS	500	172 min, mean equilibrium loss; 18°C
	Salmo gairdneri	SB, FW, LS	200	374 min, mean equilibrium loss; 18°C
	Salmo gairdneri	SB, FW, LS	20	3580 min, mean equilibrium loss; 18°C
Potassium chromate [Cr(II)]	*Nitzschia linearis* (diatom)	SB, FW, LS	0.8-0.82	120-hr TL_m
	Physa heterostropha (snail)	SB, FW, LS	16.8	96-hr TL_m; 18-22°C
	Lepomis macrochirus		168.8	96-hr TL_m, acute; 16-20°C
Potassium chromate (hexavalent chromium)	*Micropterus salmoides*	SB, FW, LS	195	48-hr TL_m, acute; 20-21°C
	Micropterus salmoides	SB, FW, LS	94	Increase, then decline in O_2 consumption; dead in 80 hr
	Oncorhynchus kisutch	CB, FW, LS	31.8	73% kill in 13 days
	Oncorhynchus kisutch	CB, FW, LS	100.0	67% kill in 5 days
	Oncorhynchus kisutch	CB, FW, LS	31.8	100% kill in 11 days
	Oncorhynchus kisutch	CB, FW, LS	31.8	33% kill in 5 days
	Oncorhynchus kisutch	CB, FW, LS	56.3	33% kill in 3 days

Table 5.7 (continued)

Chemical compound	Test organism	Test conditions[a]	Chromium concentration (ppm)	Remarks
Potassium chromic sulfate [Cr(III)]	*Daphnia magna* (cladocera)	SB, FW, LS	42	Toxicity threshold, 2 days at 23°C
Potassium dichromate	*Carassius auratus*	SB, FW, LS	100	Apparently not harmful in 108 hr, hard water
	Carassius auratus	SB, FW, LS	500	Lethal in 3 days
	Gambusia affinis	SB, FW, LS	370	24-hr TL_m, acute
	Gambusia affinis	SB, FW, LS	320	48-hr TL_m, acute
	Gambusia affinis	SB, FW, LS	280	96-hr TL_m, acute (turbid water, 21-23°C)
	Lepomis macrochirus	SB, FW, LS	739.0	24-hr TL_m, acute
	Daphnia magna	SB, FW, LS	0.4	100-hr TL_m, acute
	Physa heterostropha (snail)	SB, FW, LS	17.3	96-hr TL_m; 18-22°C
	Lepomis macrochirus	SB, FW, LS	113.0	96-hr TL_m, acute; 16-20°C
	Brachydanio rerio	SB, FW, LS	180	48-hr TL_m, acute; adults (all data at 24°C; soft water)
	Brachydanio rerio	SB, FW, LS	1500	48-hr TL_m, acute; eggs
	Brachydanio rerio	SB, FW, LS	280	24-hr TL_m, acute; adults
	Lepomis macrochirus	SB, FW, LS	440	48-hr TL_m, acute
	Snail	SB, FW, LS	17.3	TL_m, soft water, 20°C
	Snail	SB, FW, LS	40.6	TL_m, hard water, 20°C
	Lepomis macrochirus	SB, FW, LS	320	96-hr TL_m, acute; low O_2
	Lepomis macrochirus	SB, FW, LS	137	100% survival; low O_2
	Lepomis macrochirus	SB, FW, LS	320.0	96-hr TL_m, acute; small, medium, and large fish
	Lepomis macrochirus	SB, FW, LS	320.0	96-hr TL_m, acute; soft water, 18 and 30°C
	Lepomis macrochirus	SB, FW, LS	382.0	96-hr TL_m; hard water, 18°C
	Lepomis macrochirus	SB, FW, LS	369.0	96-hr TL_m; hard water, 30°C
	Lepomis macrochirus	SB, FW, LS	320	96-hr TL_m, acute (18 and 30°C), toxicity values up to 20% more in hard water
	Lepomis macrochirus	SB, FW, LS	320.0	96-hr TL_m, acute; both normal and low O_2 content
	Daphnia magna (cladocera)	SB, FW, LS	<<0.6	Highest concentration not immobilizing under prolonged exposure; 25°C
	Morone saxatilis	CB, FW, LS	150	24- and 48-hr TL_m, acute; 21.1°C, larvae
	Morone saxatilis	CB, FW, LS	100	72- and 95-hr TL_m, acute; larvae
	Morone saxatilis	CB, FW, LS	300	24-hr TL_m, acute; 21.1°C, fingerlings
	Morone saxatilis	CB, FW, LS	125	48-hr TL_m, acute; fingerlings
	Morone saxatilis	CB, FW, LS	100	72-hr TL_m, acute; fingerlings

Table 5.7 (continued)

Chemical compound	Test organism	Test conditions[a]	Chromium concentration (ppm)	Remarks
Potassium dichromate	*Morone saxatilis*	CB, FW, LS	75	96-hr TL_m, acute; fingerlings
	Lepomis macrochirus	SB, FW, LS	≅430.0	96-hr TL_m, acute, soft water; alkalinity and hardness reduced toxicity
	Pimephales promelas	SB, FW, LS	17.6 (S)[b] 27.3 (H)	96-hr TL_m, acute; in hard and soft water
	Lepomis macrochirus	SB, FW, LS	118.0 (S) 133.0 (H)	
	Carassius auratus	SB, FW, LS	37.5 (S)	
	Lebistes reticulatus	SB, FW, LS	30.0 (S)	
	Hydropsyche spp. (caddis fly)	SB, FW, LS	280	48-hr TL_m, acute soft water, 20–22°C (all data for larvae)
	Stenonema rubrum (mayfly)	SB, FW, LS	3.5	
	Salmo gairdneri	SB, FW, LS	1000	54.6 min, mean equilibrium loss; 18°C
	Salmo gairdneri	SB, FW, LS	500	60.6 min, mean equilibrium loss; 18°C
	Salmo gairdneri	SB, FW, LS	200	188 min, mean equilibrium loss; 18°C
	Salmo gairdneri	SB, FW, LS	20	4342 min, mean equilibrium loss; 18°C
Potassium dichromate [Cr(VI)]	*Daphnia magna* (cladocera)	SB, FW, LS	0.7	Toxicity threshold, 2 days at 23°C
Sodium chromate	*Gambusia affinis*	SB, FW, LS	500.0	48-hr TL_m, acute; high turbidity
	Nereis sp. (polychaete)	SB, SW, LS	0.5–10	Sublethal effect, 21 days
	Carcinus maenas (crab)	SB, SW, LS	60	12-day TL_m, acute
		SB, SW, LS	50	Sublethal effect, 12 days
	Leander squilla (prawn)	SB, SW, LS	≅10	Threshold toxicity, adults
	Leander squilla (prawn)	SB, SW, LS	≅5	Threshold toxicity, young
Sodium chromate, sodium carbonate	*Daphnia magna* (cladocera)	SB, FW, LS	0.33 408.0	50% immobilization in 100 hr, acute
Sodium chromate, sodium silicate	*Daphnia magna* (cladocera)	SB, FW, LS	0.21 130.0	100-hr TL_m; standard reference water
Sodium chromate, sodium sulfate	*Daphnia magna* (cladocera)	SB, FW, LS	0.28 3044.0	100-hr TL_m; standard reference water
Sodium chromate, sodium silicate sodium sulfate	*Daphnia magna* (cladocera)	SB, FW, LS	0.28 122.0 2255.0	100-hr TL_m; standard reference water

Table 5.7 (continued)

Chemical compound	Test organism	Test conditions[a]	Chromium concentration (ppm)	Remarks
Sodium chromate, sodium silicate, sodium sulfate	*Daphnia magna* (cladocera)	SB, FW, LS	0.201 119.0 2180.0	50% immobilization in 100 hr, acute
Sodium chromate, sodium bisulfite	*Daphnia magna* (cladocera)	SB, FW, LS	0.286 70.0	50% immobilization in 100 hr, acute
Sodium chromate, sodium bisulfite	*Daphnia magna* (cladocera)	SB, FW, LS	0.278 67.0	100-hr TL_m; standard reference water (Data on other combinations of sodium salts were provided)
Sodium chromate, sodium sulfate	*Daphnia magna* (cladocera)	SB, FW, LS	0.276 2984.0	50% immobilization in 100 hr, acute
Sodium chromate, sodium silicate	*Daphnia magna* (cladocera)	SB, FW, LS	0.159 93.0	50% immobilization in 100 hr, acute
Sodium chromate, sodium carbonate, sodium sulfate	*Daphnia magna* (cladocera)	SB, FW, LS	0.192 240.0 2079.0	50% immobilization in 100 hr, acute (Data on other three combinations of sodium salts were provided)
Sodium dichromate	*Oncorhynchus tshawytscha*	CB, FW, LS	0.08	Sublethal, survival impaired; hatchery rearing
	Salmo gairdneri	CB, FW, LS	0.013-0.022	Sublethal, growth inhibited, hatchery rearing
	Lepomis macrochirus	SB, FW, LS	500	21-hr TL_m, acute; 20°C
	Lepomis macrochirus	SB, FW, LS	410	48-hr TL_m, acute; 20°C
	Lepomis macrochirus	SB, FW, LS	76	Safe concentration
	Gambusia affinis	SB, FW, LS	420.0	48-hr TL_m, acute; turbid water
	Daphnia magna (cladocera)	SB, FW, LS	<0.31	Near immobilization in 48 hr; Lake Erie water, 25°C
	Cyprinus carpio	FW, FS (tank)	20	Survived but did not reproduce; 25°C
	Daphnia magna (cladocera)	SB, FW, LS	22.0	24-hr TL_m, acute
	Daphnia magna (cladocera)	SB, FW, LS	10.0	48-hr TL_m, acute (standard reference water)

[a] SB = static bioassay; CB = constant-flow bioassay; FW = freshwater; SW = sea (salt) water; LS = lab study; FS = field study.

[b] S = soft water; H = hard water.

Source: Adapted from U.S. Atomic Energy Commission, 1973, Table I, pp. I.3-I.10. Data collected from several sources.

Table 5.8. Sublethal doses of inorganic chromium for aquatic organisms

Species	Chronic dose (ppm)	Conditions
Daphnia magna	<0.6	Chromic acid; threshold of immobilization
	<3.6	Threshold of immobilization; chromic chloride; 64 hr
Lepomis macrochirus	728	Hydration of tissues of body due to coagulation of mucous covering body; 22.5 C; pH 5.9
Fish	0.2	Retarded rate of growth and resulted in increased mortality; hexavalent chromium
Salmo gairdneri	Not given	Change in erythrocyte surface area and increase or decrease in hematocrit value
	2-4	Raising of hematocrits
	2.5	Chromium as chromate; lab bioassay; tap water; glucose transport by gut segments reduced 40% from controls
Fish	10-50	Decreased extractable protein content of blended fish muscle

Source: Adapted from National Academy of Sciences and National Academy of Engineering, 1972, Table 2, p. 462. Data collected from several sources.

chromium levels (Sherr and Armitage, 1973). Figure 5.6 illustrates a repeating pattern of mortality, a slow rate followed by a rapid rate. The percentage of survival of 12-day-old *Daphnia* is shown in Figure 5.7. At hour 0, each group contained 40 animals. Because of the small number of animals used in this study, the results should be viewed with some reservation. The slowing of the mortality rate shown in Figure 5.7 may have been a result of the small sample size.

Warnick and Bell (1969), who examined the effects of several heavy metals on various aquatic insects, reported a 96-hr median tolerance limit (TL_m) for trivalent chromium (as chromium chloride). The water used for the studies had a temperature of 18 ± 2°C, pH 7.25, and a hardness of 44 ppm. A 96-hr TL_m value was not determined for *Acroneuria lycorias* (stone fly) because the insects did not die in 96 hr at the maximum chromium concentration tested (64 ppm). The 96-hr TL_m value was 2 ppm chromium for *Ephemerella subvaria* (mayfly) and 64 ppm chromium for *Hydropsyche betteni* (caddis fly). These results indicate that aquatic insects are not as sensitive to chromium as many fish. Analysis of water samples from polluted stretches of the Clinton River in Michigan gave hexavalent chromium concentrations as high as 25 ppm (Surber, 1959). The midgefly, *Cricotopus bicinctus*, was able to survive and reproduce in these concentrations, which indicates that it is very resistant to hexavalent chromium.

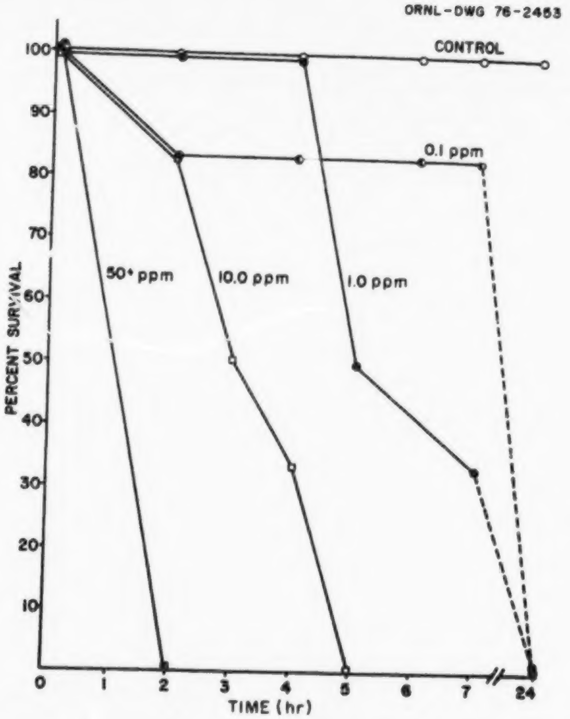

Figure 5.6. Time course of survival of *Daphnia pulex* exposed to high concentrations of sodium dichromate. Source: Adapted from Sherr and Armitage, 1973, Figure 1, p. 53. Reprinted by permission of the publisher.

The effect of temperature on hexavalent chromium toxicity was investigated using the rotifer *Philodina roseola* (Schaefer and Pipes, 1973). Median tolerance limit values for chromium at various temperatures are presented in Table 5.9. Chromium was more toxic at higher temperatures, but as exposure time increased, the effect of temperature on TL_m values was diminished. The longer the exposure time, the less effect temperature had on the chromium concentration which caused a 50% mortality rate.

Toxicity data for freshwater zooplankton were presented by Baudouin and Scoppa (1974*b*). Median lethal concentrations (at 48 hr) for *Cyclops adyssorum*, *Eudiaptomus padanus*, and *Daphnia hyalina* were 10, 10.1, and 0.022 ppm hexavalent chromium, respectively. Toxicity was measured as time for 50% mortality versus concentration of chromate. Combined temperature and concentration studies relevant to the question of the effects of thermal discharges on the uptake and toxicity of pollutants were done with one of the organisms, the copepod *Eudiaptomus*. Mortality at 15°C was higher than and parallel to that at 10°C for all concentrations; however, the curve of mortality at 20°C crossed these two and was higher than either at concentrations above about 7 ppm and lower at concentrations below about 3 ppm.

In a preliminary investigation, the crab *Carcinus maenas* was sensitive to hexavalent chromium (Raymont and Shields, 1963). A sharply defined threshold was not determined. At concentrations of 20 and 40 ppm chromium,

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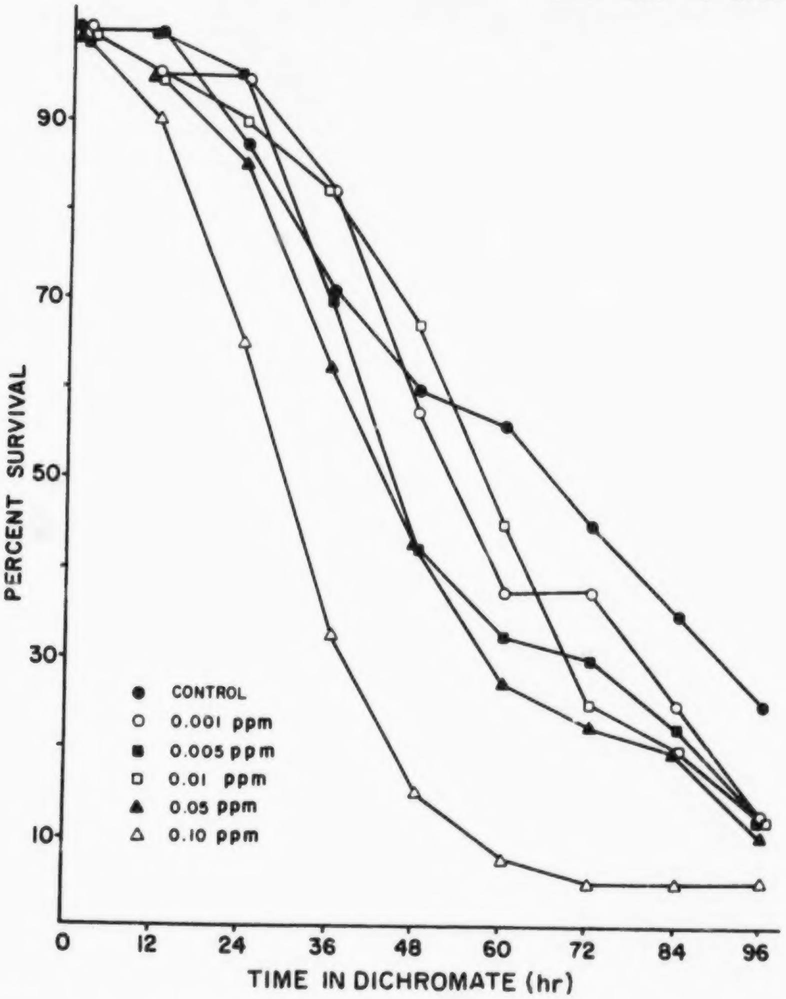

Figure 5.7. Percent survival of 12-day-old *Daphnia pulex* exposed to various concentrations of sodium dichromate. Source: Adapted from Sherr and Armitage, 1973, Figure 4, p. 59. Reprinted by permission of the publisher.

the survival rate of the exposed crabs equaled that of the controls in seawater; however, at 60 ppm chromium, a 50% mortality was reached after 12 days. The threshold level was slightly less than 5 ppm chromium for small prawns (*Leander squilla*) and 10 ppm chromium for larger prawns. A freshwater snail (*Physa heterostrapha*), a diatom (*Nitzschia linearis*), and the bluegill (*Lepomis macrochirus*) were exposed to divalent and trivalent chromium (Patrick, Cairns, and Scheier, 1968). The 96-hr TL_m was 113 ppm trivalent chromium and 168.8 ppm divalent chromium for the fish and 17.3 ppm trivalent chromium and 16.8 ppm divalent chromium for the snails. Diatoms were the most sensitive to trivalent chromium and fish were the least sensitive.

Table 5.9. Median tolerance limit values for chromate in the rotifer *Philodina roseola*

Time (hr)	Temperature (°C)	Chromate as chromium, 95% confidence limits (ppm)		
		Median tolerance limit	Lower limit	Upper limit
24	5	65	50	84
	15	43	39	52
	20	37	30	45
	25	28	23	33
	30	23	19	28
	35	18	15	22
48	5	31	27	36
	15	22	19	26
	20	18	15	21
	25	14	12	17
	30	11	9.2	13
	35	9.1	7.4	11
72	5	16	14	19
	15	12	10	14
	20	11	9.1	13
	25	7.0	5.7	8.7
	30	6.4	5.2	7.9
	35	5.3	4.5	6.3
96	5	12	10	14
	15	8.9	7.4	12
	20	7.4	6.2	9.1
	25	5.5	4.3	7.0
	30	4.4	3.5	5.6

Source: Adapted from Schaefer and Pipes, 1973, Table 3, p. 1785. Reprinted by permission of the publisher.

Salinity affects the toxicity of chromium ions (Olson and Harrel, 1973). A brackish water clam, *Rangia cuneata*, was exposed to various concentrations of hexavalent chromium at several salinities. Chromium was more toxic in fresh water than in saline water (Table 5.10) and was most toxic at a salinity of <1 ppt and least toxic at the highest salinity (22 ppt).

Calabrese et al. (1973) investigated the effect of heavy metals on oyster (*Crassostrea virginica*) embryos. Trivalent chromium as chromium chloride was relatively nontoxic as compared with mercury, silver, copper, and zinc. The LC_{50} for chromium was 10.3 ppm in water with pH 7.8 to 8.5, temperature of 26 ± 1°C, and 25% salinity.

Table 5.10. Salinity effects on median tolerance limits for chromium in the crab *Rangia cuneata*

Salinity (ppt)	Chromium ion concentration for median tolerance limit (ppm)		
	48 hr	72 hr	96 hr
<1	0.96	0.32	0.21
5.5	66.0	32.0	14.0
22	86.0	73.0	35.0

Source: Adapted from Olson and Harrel, 1973, Table I, p. 10. Reprinted by permission of the publisher.

Several workers have investigated the effects of trivalent and hexavalent chromium on fish. Chemical and physical characteristics of water affect the toxicity of chromium. Also, different fish species show varying degrees of sensitivity to chromium ions. For example, Strik et al. (1975) observed a mortality of 5 out of 20 trout after 15 days of exposure to 10 ppm chromium ($K_2Cr_2O_7$), but no mortality was observed in roach exposed to the same chromium concentration for 32 days. Mearns et al. (1976) studied relative toxicities of chromium(VI) and chromium(III) to two coastal species, the speckled sanddab (*Citharichthys stigmaeus*) and a polychaete worm (*Neanthes arenaceodentata*). Hexavalent chromium was found to be much more toxic to the marine worm than the marine fish (LC_{50} in four days of 3.1 mg/liter and 30 mg/liter, respectively). Hexavalent chromium (as $K_2Cr_2O_7$ and CrO_3) was found to be more toxic to both species than trivalent chromium (as $CrCl_3$).

In contrast to the positive effect of temperature on chromium toxicity to rotifers, Rehwoldt et al. (1972) found that temperature had no significant effect on the TL_m of trivalent chromium in several fish species. Median tolerance limit ranges were 10.3 to 31.6 ppm chromium at 15°C and 13.9 to 26.3 ppm chromium at 28°C. In water with temperature of 28°C, pH 8.0, and hardness of 55 ppm, the TL_m values for trivalent chromium at three time periods are listed in Table 5.11.

In very soft water (pH near 5.7), hexavalent chromium (as a chromate or dichromate) was much less toxic to fish than the trivalent form in simple solutions of chromic salts (Doudoroff and Katz, 1953). Concentrations below 20 ppm hexavalent chromium were nontoxic in any water; trivalent chromium was toxic at concentrations less than 2 ppm in soft water.

Table 5.11. Median tolerance limit values of trivalent chromium for several fish species

Species	Cr(III) concentration for median tolerance limit (ppm)		
	24 hr	48 hr	96 hr
Fundulus diaphanus (banded killifish)	26.3	20.8	16.9
Roccus saxatilis (striped bass)	19.3	18.8	17.7
Lepomis gibbosus (pumpkinseed)	19.1	17.8	17.0
Roccus americanus (white perch)	17.5	16.0	14.4
Anguilla rostrata (American eel)	19.5	16.3	13.9
Cyprinus carpio (carp)	21.2	18.4	14.3

Source: Adapted from Rehwoldt et al., 1972, Table II, p. 93. Reprinted by permission of the publisher.

The toxicity of hexavalent chromium to bluegills (*Lepomis macrochirus*) was investigated by Trama and Benoit (1960). Two salts, potassium dichromate and potassium chromate, were used in the study. The 96-hr TL_m was 113 ppm chromium for the dichromate and 170 ppm chromium for the chromate salts. The water had a temperature of 20 ± 1°C and a hardness of 45 ppm. When either salt was added, the pH of the water tended to shift toward neutrality. When 155 ppm potassium dichromate was added, the pH ranged from 6.3 to 6.8; with 320 ppm potassium chromate, the pH range was 7.5 to 8.5. Figure 5.8 illustrates the survival of bluegills with various concentrations of both salts. Under the test conditions, ionic partition gave more hydrochromate ion in the dichromate solution than in the chromate solution; the authors believed that the differences in TL_m values for the two salts were due to this condition. The singly charged hydrochromate ion was more readily absorbed than the doubly charged chromate or dichromate ions and was the dominant toxic species in both cases. The higher level of hydrochromate ions in the dichromate-derived solution accounted for its higher toxicity.

Several investigators have studied trout to determine the effects of chromium on fish. Garton (1973) found that with young steelhead trout no

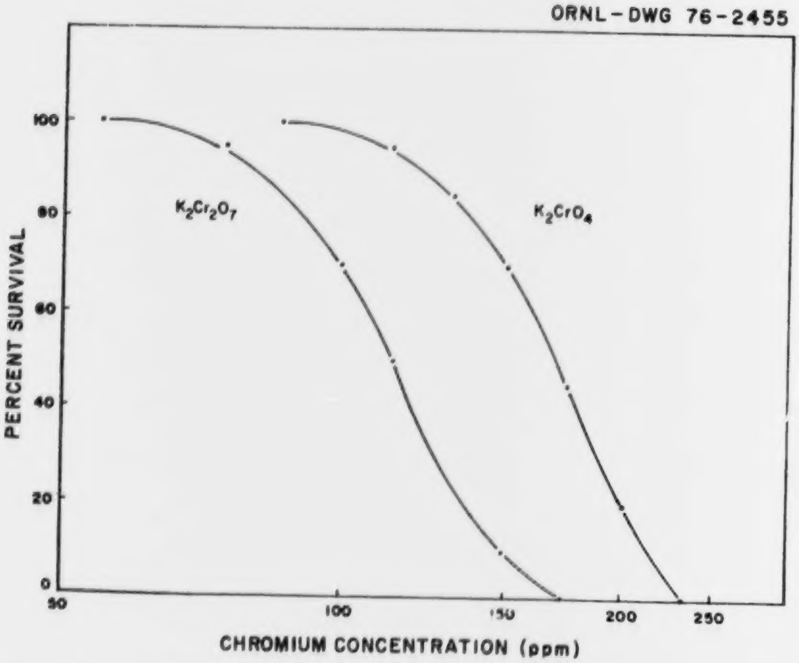

Figure 5.8. Chromium toxicity of potassium dichromate and potassium chromate to bluegills. Adapted from Trama and Benoit, 1960, Figure 2, p. 874. Reprinted by permission of the publisher.

mortalities occurred during a 96-hr exposure to 31 ppm sodium chromate (water pH, 7; hardness, 20 ppm; temperature, 10°C). Schiffman and Fromm (1959) reported a 24-hr TL_m for rainbow trout exposed to 100 ppm chromium. The water hardness was 334 ppm; temperature, 14°C to 15°C; and pH, 8.5 to 8.8 (see Section 5.3.1).

Chromium toxicity to four warmwater fish species was studied by Pickering and Henderson (1966) (Table 5.12). Soft water had pH 7.5 and hardness of 20 ppm; hard water had pH 8.2 and hardness of 360 ppm. Chromium toxicity differed for each species studied and was also influenced by water characteristics. Trivalent chromium salts formed a precipitate when they were added to the hard water, whereas hexavalent chromium did not. Because of its various hydrates, trivalent chromium was an unusual toxicant. At 48-hr, mortality of bluegills in two assays was greater at 10.41 ppm trivalent chromium than at two higher concentrations. Results showed 90% mortality at 10.41 ppm and only 20% mortality at higher concentrations. For each species in soft water, the 96-hr TL_m value was significantly lower for trivalent chromium than for hexavalent chromium. For all species, the 96-hr TL_m value was lower than the 24-hr TL_m value when hexavalent chromium was used.

These studies concerned with toxic effects of chromium on aquatic species have demonstrated that species differences, chemical and physical characteristics of water, and the form of the chromium ion all affect the action of chromium on animals. Trivalent and hexavalent chromium display different levels of toxicity, depending on species and water characteristics. Water hardness, pH, and temperature are prime considerations in determining sensitivity to chromium.

Table 5.12. Median tolerance limit values and 95% confidence limits of chromium for four species of warmwater fishes (ppm)

Salt	Dilution water	Test fish	24 hr Median tolerance limit	24 hr Confidence limits	48 hr Median tolerance limit	48 hr Confidence limits	96 hr Median tolerance limit	96 hr Confidence limits
Chromium potassium sulfate, $CrK(SO_4)_2 \cdot 12H_2O$	Soft	Fatheads	5.37	4.58-6.17	5.22	4.47-5.93	5.07	4.37-5.71
	Hard	Fatheads	77.5	65.4-102.	67.4	59.5-78.6	67.4	59.5-78.6
	Soft	Bluegills	67.4	59.5-78.6	38.7	11.4-82.8	7.46	5.56-9.84
	Hard	Bluegills	84.0	68.7-124.	71.9	62.2-88.1	71.9	62.2-88.1
	Soft	Goldfish	11.0	7.68-14.3	5.37	4.58-6.17	4.10	2.81-4.98
	Soft	Guppies	4.10	3.21-5.13	3.85	2.97-4.80	3.33	2.47-4.15
Potassium dichromate, $K_2Cr_2O_7$	Soft	Fatheads	39.6	34.6-46.6	19.7	13.6-25.6	17.6	14.0-20.9
	Hard	Fatheads	63.5	53.0-75.9	35.4	25.8-44.4	27.3	20.1-32.7
	Soft	Bluegills	284.	232.-421.	171.	137.-221.	118.	88.8-147.
	Hard	Bluegills	228.	202.-266.	180.	145.-236.	133.	103.-166.
	Soft	Goldfish	122.	107.-144.	58.3	45.1-83.3	37.5	24.4-50.9
	Soft	Guppies	133.[a]		61.7	47.4-89.0	30.0	23.0-41.2
Potassium chromate, $K_2Cr_2O_4$	Soft	Fatheads	109.	89.5-161.	60.4	46.0-81.9	45.6	32.2-59.6

[a] Value determined by graphical interpolation.

Source: Adapted from Pickering and Henderson, 1966, Table 2, pp. 456-458. Reprinted by permission of the publisher.

SECTION 5

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SECTION 6

BIOLOGICAL ASPECTS IN HUMANS

6.1 SUMMARY

Chromium is an essential trace element for humans. Total individual daily intake ranges from 5 to 115 μg. No toxic symptoms from this daily intake are known.

Chromium is absorbed through both the respiratory and gastrointestinal tracts, with hexavalent chromium being more easily absorbed in both tracts than the trivalent form. Much of the chromium ingested is not absorbed due to insolubility unless it exists as natural complexes in food (i.e., the glucose tolerance factor). In biological reactions, hexavalent chromium is reduced to the trivalent form, which coordinates with organic compounds such as nucleic acids and proteins. The hexavalent form readily penetrates the red blood cell membrane and becomes bound to the globin fraction of hemoglobin; the trivalent form, which cannot pass through the membrane, is bound to the β-globulin fraction of the plasma proteins. Trivalent chromium bound to siderophilin is thus transported to various tissues.

Chromium is consistently found in higher concentrations in the fetus and newborn than in the mother. Simple chromium compounds are not transferred across the placenta, however, the glucose tolerance factor is.

Distribution of chromium depends on its chemical state and the amount administered. Adult human tissues normally retain chromium levels ranging from 0.02 to 0.04 ppm on a dry weight basis, but levels vary with geographical distribution. Tissue chromium concentrations, except for those in the lungs, decrease with age.

In rats, three main components of elimination have half-lives of 0.5, 5.9, and 83.4 days; however, it is not known if these components are the same in humans. Urinary excretion is the major route. Small amounts are also lost through feces, and possibly the skin.

Chromium deficiency affects glucose, lipid, and protein metabolism. Supplementation with chromium improves glucose tolerance in the elderly, in malnourished children, and in noninsulin-dependent diabetics who have a chromium deficiency. Chromium affects cholesterol levels in rats, suggesting that human cholesterol levels may rise as a result of chromium deficiency.

Chromium deficiency, as evidenced by improvement of glucose tolerance with chromium supplementation, may be fairly widespread. Supplementation with chromium in a biologically available form, such as preformed glucose tolerance factor, has been recommended as a public health measure.

Chromium, particularly in the trivalent form, is not very toxic. Trivalent chromium compounds are poorly absorbed due to their insolubility. Hexavalent compounds are more toxic as a result of their oxidizing power and ease of penetration into tissues. Hexavalent chromium compounds can cause ulceration and perforation of the nasal septum, but apparently not cancer of the skin or nasal septum. A high incidence of bronchogenic carcinoma occurs in chromium chemical workers. The latent period between first exposure and disease onset is between 10 and 20 years. A dose-response relationship has not been established.

Systemic chromium poisoning effects, which include damage to the liver and tubular necrosis of the kidney, may occur from either chronic exposure or a high-exposure incident.

Threshold limit values for occupational exposure to chromium have been recommended. The maximum workplace concentration of airborne carcinogenic chromium(VI) recently recommended by the National Institute for Occupational Safety and Health is 1 $\mu g/m^3$ of breathing zone air. More stringent air quality standards for the general population can be expected because of longer exposure periods and a wider range of ages and health complications.

6.2 METABOLISM

6.2.1 Uptake and Absorption

6.2.1.1 Entry — Humans are primarily exposed to chromium through ingestion. Ingested chromium includes dietary chromium as well as inhaled chromium that is cleared to the pharynx and swallowed. Ingestion contributes the largest portion of chromium intake. A typical institutional diet provides an average of approximately 78 μg chromium per day (Schroeder, Balassa, and Tipton, 1962). Under ordinary conditions, chromium intake from air, probably less than 1 μg/day, does not contribute significantly to total intake of available chromium (National Academy of Sciences, 1974). Atmospheric chromium is mainly particulate matter in the form of trivalent chromium compounds. A small amount of chromium is absorbed through the skin, but this uptake probably occurs only through damaged skin.

Various methods for administering chromium have been used in animal studies. Chromium can be added either to the diet or to the atmosphere. Intraperitoneal, intrapleural, and subcutaneous injections, as well as implantation in tissue, allow for the introduction of chromium into a specific body area and permit greater control of chromium concentration in the animal.

6.2.1.2 Absorption — Chromium is absorbed through both the gastrointestinal and respiratory tracts. The amount absorbed differs in each system and depends on the form of chromium.

Discrepancies in values reported for chromium absorption from the digestive tract appear in the literature; exact values are not known. Trivalent chromium is poorly absorbed, whereas chromate absorption appears to be higher (Mertz, 1969). From 0.1% to 1.2% of trivalent chromium salts were absorbed, whereas 25% of glucose tolerance factor (GTF), a chromium complex necessary for normal glucose tolerance, was absorbed. Donaldson and Barreras (cited by Underwood, 1971) found that orally administered trivalent chromium was poorly absorbed regardless of dose or the dietary chromium status of the subjects. Natural chromium complexes in the diet seem to be more available for absorption than simple salts. The contents of the digestive tract can influence the amount of chromium absorbed; the presence of foods may decrease chromium absorption.

Acid gastric juice reduces hexavalent chromium ions to trivalent chromium ions, which are poorly absorbed (Underwood, 1971). The mechanism by which chromium is carried across the intestinal wall and the site of absorption are not known (Mertz, 1969). Chromium can precipitate in the form of large, insoluble complexes if it is not protected from the alkaline intestinal contents by coordination. The degree of absorption may depend on how efficiently suitable ligands protect against olation (Section 2.2.6.1).

Chromium absorption through the respiratory tract can be as complicated as absorption through the digestive tract. The absorption of chromic compounds is slightly greater through the respiratory tract than through the digestive tract (Baetjer, 1956). Absorption of inhaled chromium seems to occur through one of three mechanisms (National Academy of Sciences, 1974). Inhaled chromium with a particle size greater than 1 μ is usually trapped in the bronchi and does not enter the alveoli (Schroeder, 1970). These particles are moved by ciliary action and swallowed (National Academy of Sciences, 1974). Pulmonary chromium may be in either soluble or insoluble form (Schroeder, 1970). Insoluble particles small enough to penetrate into the alveoli can be trapped in tissue; soluble particles penetrate into the blood to be distributed throughout the body. Water- and serum-soluble chromates are absorbed into the blood system, whereas insoluble trivalent chromium particles and relatively inert oxides and hydroxides of trivalent chromium remain in lung tissue.

6.2.2 Transport

6.2.2.1 Transport in Blood — Chromium compounds are bound by proteins in the blood (Gray and Sterling, 1950). Intravenously injected anionic hexavalent chromium passes through the membrane of red blood cells and binds to the globin fraction of hemoglobin. Gray and Sterling (cited in Baetjer, 1956) hypothesized that before hexavalent chromium is bound by hemoglobin, it is reduced to trivalent chromium by an enzymatic reaction within red blood cells. Once inside the blood cell, chromium ions are unable to repenetrate the membrane and move back into the plasma. In physiological amounts, cationic trivalent chromium is bound to siderophilin and transported to other tissues (Hopkins and Schwarz, 1964). The distribution in plasma protein fractions is dose dependent. Large concentrations of chromium ions saturate the binding sites of siderophilin and will then bind to other proteins, but not in red blood cells.

Subsequent tissue uptake depends on the chemical state of chromium (Visek et al., cited in Mertz, 1969). Acetate and citrate complexes are efficiently excreted, whereas chromite and chromic chloride, which are colloidal or protein bound, give rise to a high chromium concentration in tissues. Chromium disappears quickly from the blood and is taken up by other tissues, where it is 10 to 100 times more concentrated than in the blood (National Academy of Sciences, 1974). Therefore, blood chromium concentration is not a good indicator of chromium nutritional status (Mertz, 1969). Furthermore, various tissues retain chromium longer than plasma does; hence, there is no equilibrium between tissue-stored and circulating chromium (Underwood, 1971).

6.2.2.2 Placental Transfer — Chromium has been found consistently in the fetus and newborn (Mikosha, cited in National Academy of Sciences, 1974). In the human fetus, the chromium concentration increases at 2.5 to 7 months (Mikosha, cited in Mertz, 1969). Following this increase, the chromium concentration shows a sharp drop at birth.

The chromium concentration in newborn rats was not increased by feeding the mother chromium chloride in drinking water, but the concentration was increased by natural sources of chromium in the diet (Mertz et al., 1969). Results from intravenous injection of one dose of [^{51}Cr]chromic chloride (5 μCi per rat) at the time of mating indicated that none of the ^{51}Cr in the mother was lost to the young at birth. Repeated doses of salt administered by stomach tube throughout pregnancy produced a small amount of labeled chromium in the offspring. However, ^{51}Cr extracted from brewer's yeast and fed to pregnant rats by stomach tube was transported into the fetus. These results indicated active transport of chromium across the placenta against a gradient. Fetal chromium must be derived from specific chromium complexes in the diet. It has been demonstrated that chromium is transported into the fetus in the glucose tolerance factor (National Academy of Sciences, 1974).

6.2.3 Distribution

Chromium is distributed in human tissues in variable, low concentrations. Chromium analysis has not been standardized; therefore, caution should be used in comparing chromium concentrations in human tissues, especially in comparing results from different laboratories. Distribution of administered chromium depends on chemical state and amount given; it is not certain whether the affinity of chromium for certain body systems, such as the reticuloendothelial system, is due to a physiological dependency or to an overload of the system (National Academy of Sciences, 1974). The affinity of chromium for the reticuloendothelial system as well as for the spleen, liver, and bone marrow probably represents phagocytosis of the colloidal particles (Mertz, 1969). The accumulation of radiolabeled chromate in the spleen may represent the chromium bound to red blood cells. Chromium levels in tissues other than the lungs decline with age. The chromium concentration in the lungs increases in later life because of the deposition of insoluble chromium by inhalation. Schroeder, Balassa, and Tipton (1962) found that chromium levels in the heart, lung, aorta, and spleen decrease during the first ten years of life; liver and kidney levels remain stable until the second decade, when a decrease occurs. In studying trace metal content in coronary arteries of Nigerians, Taylor and Williams (1974) found that chromium levels decreased with age in males but not in females.

6.2.3.1 Administered Chromium Distribution in Rats and Guinea Pigs — Schroeder and Nason (1974) found that adding 5 ppm chromium to drinking water significantly increased chromium levels in the lung, heart, and kidney of rats (Table 6.1). Increased chromium concentrations were found in the spleens of these rats compared to those in rats given plain water and basal water containing manganese, cobalt, copper, zinc, and molybdenum. The heart and spleen concentrated chromium when the sole source was dietary intake. The feeding of cadmium and its subsequent accumulation appeared to suppress chromium levels in the heart and in male kidneys.

High chromium levels in the heart, lung, and kidney of mature and immature rats were also reported by Hopkins (1965). Chromium-51 trichloride at concentrations of 0.001 and 0.1 ppm body weight was injected intravenously. Dose level, diet, and sex had no effect on tissue distribution. Tissue retention differed among various organs. At four days after injection, the heart, lungs, pancreas, and brain retained 10% to 31% of initial radioactivity, whereas the spleen, kidney, testis, and epididymis concentrated chromium and had 104% to 200% activity. The brain had the least affinity for chromium. Chromium levels of mature rats were higher than those of immature rats in the spleen, kidney, testis, and epididymis; immature animals showed higher chromium levels in the bones. The mature testis took up chromium more than any other organ; during the 4-hr period following injection, accumulation increased 400%.

Water-soluble chromate injected intratracheally was retained only slightly (15%) in the lungs of guinea pigs, whereas 69% of chromic chloride was retained (Baetjer, Damron, and Budacz, 1959). Thus, trivalent chromium was retained in the lungs longer and at a higher level than hexavalent chromium (Figure 6.1). Chromium retained in both animal and human lung tissues was present either in a hydrated or acid-soluble form which was absorbed by cell membranes or cellular debris or was combined with nuclei. The lung tissue of humans possesses the same ability to bind chromium as that of guinea pigs.

6.2.3.2 Distribution in Human Organs — Adult human tissues generally contain 0.02 to 0.04 ppm chromium on a dry weight basis (Underwood, 1971). Several investigators have studied chromium distribution in healthy human tissues (Table 6.2).

Chromium levels in human liver and kidneys vary with geographic location (Schroeder, Balassa, and Tipton, 1962). Chromium was not detected in the liver and kidneys of some Americans but was found in the liver and kidneys of all foreigners examined. Foreigners had higher chromium levels than Americans in all tissues except lung tissue of Far Eastern subjects, heart and lung tissues of Near Eastern subjects, and aorta, kidney, pancreas, and testis tissues of Swiss subjects (Table 6.3) (Schroeder, 1970). These data indicate that Americans may be deficient in chromium.

A mean concentration of 0.22 ppm chromium (wet wt) was found in lung tissue of subjects from various locations in the United States (Schroeder, 1970). A rough correlation existed between chromium levels in lungs and in air from 1954 to 1959. Tipton and Shafer (cited in Schroeder, 1970)

Table 6.1. Chromium concentrations in the organs of rats given plain water, basal water without chromium, and basal water with chromium

Type of water	Number of rats/ number of samples	Median age (days)	Chromium intake, diet + water (ppm)	Chromium in organs (ppm)[a]				
				Liver	Lung	Heart	Kidney	Spleen
Plain water	23/12	360	0.14 + 0	0.19 ± 0.015	0.47 ± 0.664	1.27 ± 0.235	0.57 ± 0.442	2.02 ± 0.357
Basal water without chromium	31/6	838	0.14 + 0	0.15 ± 0.053	0.20 ± 0.031	0.48 ± 0.031	0.51 ± 0.233	1.33 ± 0.466
Basal water with 5 ppm chromium	66/11	863	0.14 + 5	0.49 ± 0.197	2.14 ± 0.795	2.30 ± 0.673	2.47 ± 0.555	3.01 ± 1.090

[a] Values for both sexes combined.

Source: Adapted from Schroeder and Nason, 1974, Table 2, p. 171. Reprinted by permission of the publisher.

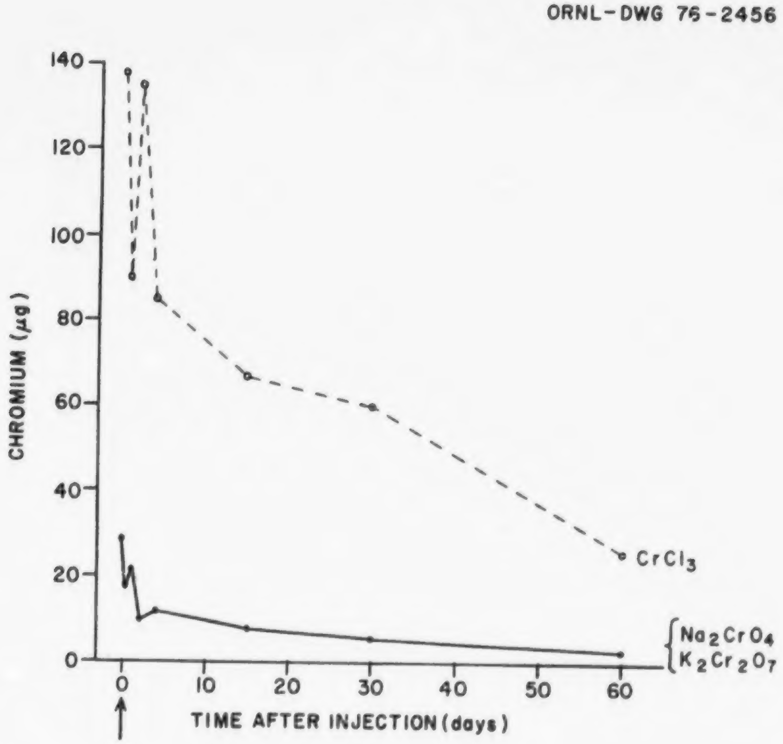

Figure 6.1. Micrograms of chromium in lungs of guinea pigs after intratracheal injections of 200 μg of chromium as trivalent chromic chloride or chromates. Source: Adapted from Baetjer, Damron, and Budacz, 1959*a*, Figure 2, p. 60/142. Reprinted by permission of the publisher.

also found significant correlations between levels of chromium and levels of aluminum, titanium, and vanadium in lungs.

Sanders et al. (1971) studied the distribution of chromic oxide particles in pulmonary alveoli by exposing hamsters to chromic oxide dust (0.5 to 1.0 ppm in air for 4 hr). Large numbers of chromic oxide aggregates were free in the alveolar lumens or within the alveolar epithelium, the granular pneumonocytes. The median diameter for the chromic oxide particles was 0.17 μm. Over 90% of the oxide was found in macrophages and 4% was found in type I alveolar epithelium.

6.2.3.3 Distribution in Blood and Urine — A wide range of values for chromium content in blood and urine has been reported. Analysis of low chromium concentrations in blood and urine has not been standardized; therefore, these values should be regarded with caution (National Academy of Sciences, 1974). Schroeder, Balassa, and Tipton (1962) reported chromium levels of 0.52 and 0.17 ppm in serum, whereas Doisy et al. (cited in National Academy of Sciences, 1974) found a chromium concentration of only

Table 6.2. Chromium concentrations in human tissues

Tissue	Chromium concentration (ppm) Ash wt	Wet wt	Reference
Adrenal	9.4		Tipton and Cook, 1963
Aorta	0.1-56.0		Tipton, 1960
	2		Tipton and Cook, 1963
Bladder	3.4		Tipton and Cook, 1963
Bone	<0.1		Tipton and Cook, 1963
Brain	0.2		Tipton and Cook, 1963
		0.01	Hamilton, Minski, and Cleary, 1973
	<0.1-3		Tipton, 1960
Cecum	6.2		Tipton and Cook, 1963
Diaphragm	2.3		Tipton and Cook, 1963
Duodenum	2.3		Tipton and Cook, 1963
Esophagus	3.0		Tipton and Cook, 1963
Fat	3.2		Tipton and Cook, 1963
Heart	1.5		Tipton and Cook, 1963
	0.1-3.9		Tipton, 1960
	0.005-0.075		Wester, 1972
Ileum	4.0		Tipton and Cook, 1963
Jejunum	1.7		Tipton and Cook, 1963
Kidney	1.0		Tipton and Cook, 1963
	<0.1-19		Tipton, 1960
	2.3		Schroeder, Balassa, and Tipton, 1962
		0.03	Hamilton, Minski, and Cleary, 1973
Larynx	0.1		Tipton and Cook, 1963
Liver	0.7		Tipton and Cook, 1963
	<0.1-15		Tipton, 1960
	1.6		Schroeder, Balassa, and Tipton, 1962
		0.08	Hamilton, Minski, and Cleary, 1973
Lung		0.5	Hamilton, Minski, and Cleary, 1973
	13		Tipton and Cook, 1963
	0.5-115		Tipton, 1960
Lymph node		2.2	Hamilton, Minski, and Cleary, 1973
Muscle		0.005	Hamilton, Minski, and Cleary, 1973
	1.0		Tipton and Cook, 1963
Omentum	12		Tipton and Cook, 1963

Table 6.2 (continued)

Tissue	Chromium concentration (ppm) Ash wt	Chromium concentration (ppm) Wet wt	Reference
Ovary	2.2		Tipton and Cook, 1963
	0.1-510		Tipton, 1960
		0.06	Hamilton, Minski, and Cleary, 1973
Pancreas	1.6		Tipton and Cook, 1963
	0.2-100		Tipton, 1960
Prostate	0.9		Tipton and Cook, 1963
	0.1-8		Tipton, 1960
Rectum	4.1		Tipton and Cook, 1963
Sigmoid colon	3.9		Tipton and Cook, 1963
Skin	17		Tipton and Cook, 1963
Spleen	0.5		Tipton and Cook, 1963
	<0.1-8		Tipton, 1960
Stomach	2.0		Tipton and Cook, 1963
Testis	1.6		Tipton and Cook, 1963
	0.1-18		Tipton, 1960
		0.03	Hamilton, Minski, and Cleary, 1973
Thyroid	1.5		Tipton and Cook, 1963
Trachea	3.4		Tipton and Cook, 1963
Uterus	1.6		Tipton and Cook, 1963

2 ppb in serum. Chromium values found by others (cited in Underwood, 1971) ranged from 0.011 to 55 ppb in human plasma and from 5 to 54 ppb in red blood cells. Imbus et al. (1963) found blood chromium levels ranging from 13 to 55 ppb with a median of 27 ppb for U.S. subjects, while Hamilton, Minski, and Cleary (1973) reported a blood level of 70 ppb chromium for subjects from the United Kingdom. Hambidge (cited in National Academy of Sciences, 1974) found chromium levels in urine of 8.4 ppb for adults and 5.5 ppb for children over a 24-hr period. Imbus et al. (1963) reported urinary levels from 1.8 to 11 ppb chromium with a median of 2.77 ppb.

6.2.3.4 Distribution in Hair — As reported by Schroeder and Nason (1969), chromium concentrations in hair were relatively constant with age rather than duplicating the pattern of decreased amounts of chromium in tissues. Levels were similar for both males and females; the mean chromium concentrations were 0.69 ± 0.063 ppm for men and 0.96 ± 0.049 ppm for women.

Hambidge, Franklin, and Jacobs (1972) measured chromium concentrations in hair at various distances from the root. They found that the concentration did not depend on the time the hair had been exposed to the external

Table 6.3. Geographical distribution of chromium in human tissues[a] (ppm, ash)

Tissue	United States	Africa	Near East	Far East	Switzerland
Aorta	1.9	5.5	11[b]	15[b]	8.8[b]
Brain	0.2	0.6	2.4[b]	2.7[b]	1.9
Heart	1.6	0.9	4.0	6.3[b,c]	4.6
Kidney	0.8	2.0	5.3[b,c]	3.3[b]	2.5[b]
Liver	0.8	1.3	2.1[b]	2.0[b]	2.9
Lung	14	16	22	23	62
Pancreas	1.6	2.5	4.2[b]	6.7[b]	5.9[b]
Spleen	0.5	1.3	3.1[b,c]	3.1[b,c]	4.5
Testis	1.6	4.2	7.0[b]	8.3[b]	7.3[b]

[a] Males, ages 20 to 59, median values.
[b] Differs from U.S. values, $P < 0.001$.
[c] Differs from African values, $P < 0.001$.

Source: Adapted from Schroeder, 1970, Table 7, p. 12. Reprinted by permission of the publisher.

environment, but that concentration changes were due to past fluctuations in chromium nutritional status. However, in disagreement with Hambidge, Franklin, and Jacobs (1972), Creason et al. (1975) reported that chromium levels in children's hair were significantly associated with environmental exposure gradients.

Hambidge and Rodgerson (1969) found higher chromium levels in hair of nulliparous women (0.2 to 2.81 ppm) than in hair of parous women (0.04 to 1.14 ppm), though a later study (Hambidge and Droegnueller, 1974) found changes in hair concentrations due to pregnancy that were not statistically significant. Mahalko and Bennion (1976) used furnace AA to obtain values for hair chromium concentrations of nulliparous and parous women who had just given birth. Mean hair chromium concentrations of nulliparous and parous women were 309 ± 23 and 117 ± 10 ppb, respectively. No further significant decrease in hair chromium was observed in women who had borne more than one child. It was observed that hair chromium concentration increased significantly with the amount of time between pregnancies, especially when at least four years had passed since the end of the last pregnancy. The data suggest a state of suboptimal chromium nutrition during pregnancy. A study of hair chromium concentrations of children revealed that chromium levels in 3- to 8-month-old infants were significantly higher than in those of 2- to 3-year-old children (Hambidge and Rodgerson, 1969). Mean chromium levels in hair declined during the latter part of the first year and during the second year approached levels present in older humans (Table 6.4).

Table 6.4. Mean hair chromium concentrations of human subjects ages 0 to 35 months

Age of subjects	Number of subjects	Hair chromium concentration (ppb)[a]
0-7 days	25	910 ± 139
3-6 months	6	1493 ± 386
8 months	8	850 ± 106
10-12 months	11	631 ± 62
1-2 years	23	525 ± 59
2-3 years	20	412 ± 47

[a] Mean ± standard error of the mean.

Source: Adapted from Hambidge and Baum, 1972, Table 1, p. 277. Reprinted by permission of the publisher.

6.2.4 Chromium Interactions

The solubility of trivalent chromium in biological material is based on the variety of small compounds which coordinate to chromium in biological fluids (Rollinson, 1966). In the absence of ligands, olation would cause the formation of large chromic hydroxide complexes of a colloidal nature with no biological activity. Ligands in the intestines prevent olation and precipitation, keep chromium soluble, and make it available for absorption.

6.2.4.1 Proteins — The tanning process is the best-known interaction of chromium with proteins. Hexavalent chromium is reduced to trivalent chromium, which is then coordinated to carboxyl groups of collagen strands (Mertz, 1969). However, chrome tanning is a total saturation of protein with chromium and does not occur at physiological chromium concentrations. At these concentrations (100 ppm), chromium cross-links protein without tanning. Trivalent chromium strongly binds to egg protein and human plasma proteins (Grogan and Oppenheimer, 1955). Hexavalent chromium, however, reacts with protein through weak bonds only at low pH.

6.2.4.2 Enzymes — Chromium inhibits enzyme reactions when concentrations excessive for a particular enzyme are added in vitro. Either trivalent or hexavalent chromium inhibits thromboplastic activity (Chargaff and Green, cited in National Academy of Sciences, 1974) and β-glucuronidase activity (Fernley, cited in National Academy of Sciences, 1974). Amounts of chromium exceeding saturation levels of the specific receptor site react with other sites, and if these sites are essential to activity, a depression of function will result (Mertz, 1969). Chromium seems to be an integral part of the digestive enzyme trypsin (Langbeck et al., cited in National Academy of Sciences, 1974). Removing chromium from trypsin resulted in a loss of activity which was restored by adding chromium.

Chromium also has the ability to stimulate enzyme activity. Horecker et al. (cited in Mertz, 1969) found that trivalent chromium stimulated oxygen consumption in a succinic dehydrogenase-cytochrome system. The enzyme phosphoglucomutase, which functions in glucose metabolism, is stimulated by chromium (Strickland, cited in Mertz, 1969), as is the conversion of acetate to carbon dioxide, cholesterol, and fatty acids by rat liver in vitro (Curran, cited in Mertz, 1969).

6.2.4.3 Nucleic Acids — Hexavalent chromium has been shown to react with nucleic acids. Tissues treated with chromate become green, which suggests that the reaction is a reduction from hexavalent to trivalent chromium followed by complex formation with nucleic acids (National Academy of Sciences, 1974). Nucleic acids contain high chromium concentrations. Analysis of beef heart tissue and ribonucleic acid (RNA) for trace elements showed that chromium in RNA was enriched by several times over chromium in whole heart tissue (Wester, 1972). Chromium levels in RNA ranged from 0.049 to 6.0 ppm. Wacker and Vallee (1959) found the chromium content of RNA from calf pancreas, calf thymus, horse kidney, rabbit reticulocytes, and rat liver to be 140, 77, 180, 140, and 630 ppm, respectively. Chromium is very firmly bound to RNA; it possibly plays a role in maintaining the configuration of the RNA molecule by linking purine and pyrimidine bases through covalent bonds.

6.2.4.4 Other Trace Elements — Schroeder and Nason (1976) found that chromium levels were depressed in heart, kidney, and spleen when germanium was administered and elevated in these same tissues by indium and rhodium. Feeding of hexavalent chromium elevated chromium levels in all tissues except the heart.

6.2.5 Elimination

6.2.5.1 Biological Half-life — The excretion of trivalent chromium measured by whole-body counting is independent of the amount administered and the chromium dietary status (Mertz, Roginski, and Reba, 1965). In rats, three main components of the retention curve have half-lives of 0.5, 5.9, and 83.4 days. In humans, chromium turnover appears to be very slow (National Academy of Sciences, 1974). The estimated fraction of chromium absorbed by man through ingestion (International Commission on Radiological

Protection, 1966) is similar (<0.005) to the fraction assimilated by native cotton rats (0.008) (Taylor, 1975). Similarly, the biological half-times of the fraction (long component) assimilated by man and cotton rats are 616 and 693 days, respectively. If humans have the three-component excretion rate, the first component may be an effective way of rapidly eliminating excess chromium.

6.2.5.2 Routes of Elimination — Chromium is excreted in both urine and feces. Urinary excretion is the major route with at least 80% of injected chromium excreted in this manner (Mertz, 1969). The intestine plays only a minor part in chromium elimination. Visek et al. (1953) found that rats eliminated up to 20% of intravenously injected trivalent chromium in feces. The site of chromium excretion in the intestines is not known. Reported ranges of daily chromium excretion in urine vary; a representative range of 1.6 to 21 ppb chromium was reported by Hambidge (1971).

Colling et al. (cited in Mertz, 1969) studied urinary excretion in dogs following intravenous injection of chromium. Chromium coordinated to small molecular ligands was filtered at the glomerulus; however, up to 63% was then reabsorbed in the tubuli from the filtrate. Only a very small portion of protein-bound chromium is excreted; almost all urinary chromium is in a dialyzable form. Urinary excretion of injected chromium (0.1 μg chromium per 100 g body wt) in male rats had two components over a four-day period (Figure 6.2) (Hopkins, 1965). Only 6% to 7% of injected trivalent chromium was excreted in the feces.

Davidson, Burt, and Parker (1974) studied the effect of a standard glucose load or a water load on the renal excretion of chromium in normal subjects. A standard glucose load (75 g) resulted in a significant decrease in the urinary excretion of chromium in fasting rats. A water load increased excretion by more than 100% due to diuresis.

6.3 EFFECTS

Chromium is necessary for glucose and lipid metabolism and for utilization of amino acids in several mammalian systems. It is also important in the prevention of common chronic diseases such as mild diabetes and atherosclerosis in humans.

6.3.1 Effects on Biochemical Systems

Table 6.5 summarizes the effects of chromium on several biochemical systems and functions.

6.3.1.1 Glucose Metabolism — Chromium is involved in glucose metabolism as part of the glucose tolerance factor (GTF). This factor is a naturally occurring chromium complex that is found in brewer's yeast and other foodstuffs. The complex itself has not been completely identified, although partial characterization has been achieved (Mertz, 1974, 1975; Mertz et al., 1974; Polansky, 1974; Toepfer, 1974; Toepfer et al., 1973, 1977). These investigators postulate that the primary configuration of the glucose tolerance factor is a niacin-Cr-niacin axis. A suggested structure of the

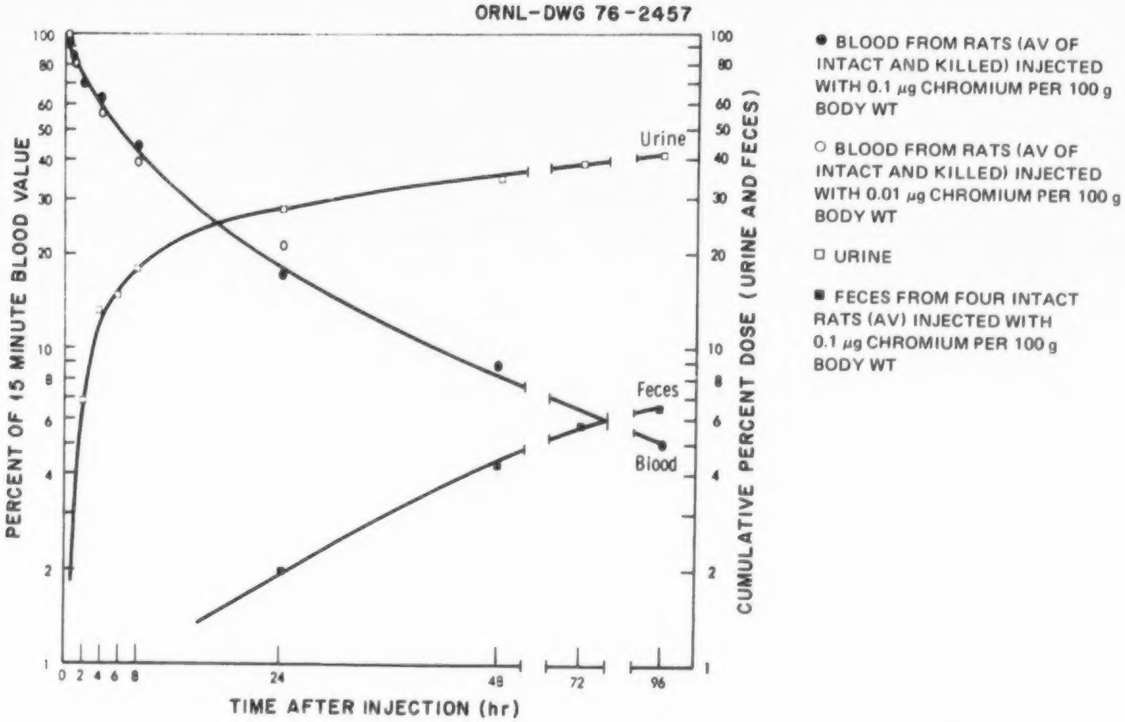

Figure 6.2. Rate of urinary and fecal excretion and blood clearance of intravenously injected trivalent ^{51}Cr from male rats. Source: Adapted from Hopkins, 1965, Figure 1, p. 733. Reprinted by permission of the publisher.

complex is shown in Figure 6.3. Toepfer et al. (1977) and Mertz et al. (1974) have also synthesized a material which possesses almost identical chemical and biological characteristics as glucose tolerance factor extracted from brewer's yeast. Detection of nicotinic acid, chromium, glycine, glutamic acid, and cysteine in GTF extracted from brewer's yeast led to this synthesis.

The glucose tolerance factor is required for normal glucose tolerance and appears to act by potentiating the action of insulin. In animals whose diets are deficient in chromium, glucose is removed from the bloodstream only half as fast as it is normally removed. This impairment is the first sign of chromium deficiency. With long-term deprivation, additional complications may develop (Mertz, 1969), including impaired growth, aortic and corneal lesions, and reduced life span. The GTF appears in certain foods and is especially rich in brewer's yeast, which results in quick relief of impaired glucose tolerance when added to the diet. Feeding with chromium compounds may also relieve impairment of glucose tolerance. In the experiments of Schwarz and Mertz (1959) which led to the discovery of chromium as the active element in GTF, feeding with a number of trivalent

Table 6.5. Biochemical actions of chromium

System or function	Animal	Deficiency state	Effect of chromium
Glucose metabolism			
Glucose tolerance	Rat, monkey	Reduced	Restored
Diabetic state	Rat	Induced	Cured
Insulin response	Rat	Reduced	Restored
Blood glucose	Rabbit, mouse	Elevated	Lowered
Glycogen formation	Rat	Delayed	Increased
Glucose tolerance	Man		Restored to normal
Glucose tolerance	Man (diabetes)		Slightly improved
Lipid metabolism			
Cholesterol synthesis	Rat	$+^a$	Increased
Fatty acid synthesis	Rat	+	Increased
Serum cholesterol	Rat	Elevated	Reduced
Serum cholesterol	Man	Elevated	Slightly reduced
Aortic lipids and plaques	Rat	Increased	Prevented and lowered
Amino acid metabolism			
Protein synthesis, growth	Rat, mouse	Reduced	Increased
Utilization	Rat	Reduced	Increased
Survival and life span	Mouse, rat	Reduced	Increased
Eye	Rat	Corneal opacity	Prevented

[a] + indicates animal is capable of synthesis.

Source: Adapted from Schroeder, 1970, Table 14, p. 18. Reprinted by permission of the publisher.

chromium compounds at a level of 20 to 50 μg chromium per 100 g body weight resulted in overnight improvement of glucose tolerance. However, only a small part of most complexes is absorbed; equivalent improvement was achieved in 2 hr by intravenous injection of only 0.25 to 0.50 μg chromium, as the neutralized chrome alum complex, per 100 g of rat body weight (Mertz, Roginski, and Reba, 1965).

Relief of impaired glucose tolerance by feeding of chromium has also been shown in other animals. For instance, trivalent chromium (10 ppm) as the acetate added to drinking water relieved impairment of glucose tolerance in squirrel monkeys which were chromium deficient (Davidson and Blackwell, 1968). The glucose removal rate per minute was 1.38% before chromium supplementation and 2.23% after supplementation. The effect of chromium depended on the valence state and apparently also on the chemical form of the trivalent state. Divalent chromium given to monkeys with normal glucose tolerance caused an impairment of tolerance. The authors suggested that the divalent chromium may have interfered with either the absorption of the trivalent chromium (which is the biologically active form) or its effect at the cellular level. Trivalent chromium given at acid pH was not effective in relieving impairment; the authors postulated that this was due to formation of complexes which were poorly absorbed.

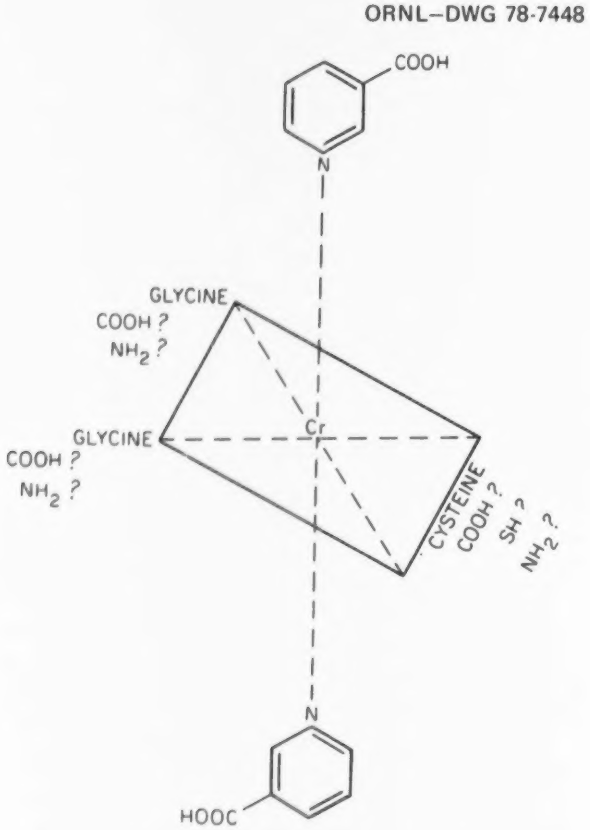

Figure 6.3. Possible structure for the glucose tolerance factor. Source: Adapted from Mertz et al., 1974, Figure 4, p. 2279. Reprinted from Federation Proceedings 33:2275-2279, 1974.

Three levels of dietary chromium (0.125, 0.625, and 50 ppm) were fed to nonpregnant, pregnant, and F-1 offspring guinea pigs by Preston et al. (1976). All groups had similar weight gain patterns and dietary intake levels. Mortality rates during pregnancy were less for pigs fed the two higher chromium levels than for those on the base diet. Glucose tolerance, glucose peak time, and serum cholesterol appeared to be more affected by pregnancy and generation of guinea pigs than by the levels of dietary chromium.

Chromium also plays an important role in human glucose metabolism. In a study by Levine, Streeten, and Doisy (1968), chromium supplementation (150 μg daily) was given orally over a period of two to four months to ten elderly human subjects who were apparently healthy and who had no family history of diabetes but whose oral glucose tolerance tests were abnormal. In four of these subjects glucose tolerance became normal, but in six it remained abnormal. Insulin and insulin-like activity levels in all the subjects were normal and rose normally in response to the glucose loads.

Thus, the beneficial effect of the chromium in the glucose tolerance responders did not result from an increased release of insulin. Significantly, the serum chromium concentrations increased in response to glucose load in both old and young (control group subjects), but the increase was less in the elderly nonresponders. These results suggest that an adequate rise in serum chromium might be necessary for a normal response to glucose. In direct contrast to these observations, however, Pekarek et al. (1975) found a precipitous fall in serum chromium (1.50 to 0.85 ppb) on administration of a 30 g intravenous glucose load. Analytical uncertainty may contribute to this contradiction.

In analyzing studies such as the above, Underwood (1971) hypothesized that patients respond by improved glucose tolerance when their low-chromium state has not been irreversibly complicated by other factors. If tissue stores of chromium have been long depleted, supplementation for longer periods than in the above study might be needed for a threshold of response to be reached. Levine, Streeten, and Doisy (1968) noted that the group which responded had a much milder impairment than the nonresponders, which implicates damage as the chief reason for nonresponse. However, depletion not relieved in the time period of the trial could also have been a factor in the lack of response of some subjects in the nonresponding group. Poor absorption and deficient synthesis of GTF are other possible reasons for lack of response to chromium supplementation.

Clearance of glucose from the blood in the glucose tolerance test depends on uptake of glucose into cells. Chromium has been shown to interact with insulin in this process. Using epididymal fat tissue of rats fed GTF-deficient diets, Mertz, Roginski, and Schwarz (1961) showed up to 94% increases in uptake of glucose and incorporation of glucose carbon into the tissue after small amounts of chromium were added. The presence of insulin was indispensable. Insulin alone was without effect. In experiments using D-galactose as substrate (Mertz and Roginski, 1963), addition of 0.01 μg chromium per 100 mg tissue increased entry rates of the sugar by a factor of 3.8 over controls in the presence of 1 milliunit of insulin. Again, neither chromium nor insulin alone was effective. While galactose is metabolized in the liver, it is poorly metabolized in peripheral tissues; hence, these results indicate that the chromium with insulin acts at the level of sugar entry into the cells from the extracellular fluid.

Chromium is involved in other insulin-sensitive processes, including the oxidation of glucose, utilization of glucose for lipogenesis, swelling of mitochondria, and incorporation of certain amino acids into proteins (Mertz, 1974). These and other actions of insulin (activation and induction of some enzymes, inhibition of other enzymes, inhibition of lipolysis) may not be as unrelated as they seem. Insulin acts in a generalized manner on the plasma membrane of the target cells, which causes changes that lead to enhanced entry not only of glucose and other sugars but also of amino acids, lipids, and the potassium ion (Lehninger, 1975). This action is followed by increased synthesis of protoplasm and storage products.

On the basis of polarographic shifts observed in experiments with liver mitochondria, Mertz (1967, 1969) postulated that chromium could act as a catalyst in the initial reaction between insulin and specific membrane sites. A ternary complex would be formed that would facilitate the disulfide interchange between membrane sulfhydryls and disulfide bonds of insulin that have been postulated by some authors (Cadenas et al., 1961; Fong et al., 1962) as being part of the mechanism of insulin action. It is not clear whether chromium acts as a simple compound, an extended complex, or as part of GTF. Some studies on the metabolism of chromium have suggested that it may act as a simple compound (Mertz, 1974); however, the effect of GTF is always greater and it is likely that chromium, to be fully effective, must be part of a GTF complex. According to Hopkins (1971), following absorption and transport, GTF is stored in a pool before it responds to a glucose load. Inorganic trivalent chromium taken in as part of the diet is transported to various metabolic sites, one of which is the site of GTF synthesis. The synthesized GTF then joins the storage pool for utilization. Hopkins hypothesized that persons who do not respond to chromium supplementation may be deficient in the ability to synthesize GTF. It is not known if mammals are capable of GTF synthesis. If the capability exists, either in the mammal itself or in its intestinal flora, it does not seem to be very efficient in the majority of adults and may be the limiting factor in chromium metabolism (Mertz, 1974).

6.3.1.1.1 Hypoglycemia — In a severe chromium deficiency state, rats and mice showed glycosuria and hypoglycemia (Mertz, 1967). Mertz and Roginski (cited in Mertz, 1969) found that rats injected subcutaneously with 100 milliunits of insulin per 100 g body weight had a hypoglycemic response which was significantly less than that of chromium-supplemented controls. Incorporation of glucose carbon 1 hr after injection of 1 milliunit of insulin per 100 g body weight was greater in chromium-supplemented rats than in nonsupplemented rats. Rats raised in conditions of maximal chromium exclusion had fasting hypoglycemia and glycosuria (Schroeder, cited in National Academy of Sciences, 1974). Half of the chromium-deficient rats had a positive test for urine sugar, whereas 9 of 87 chromium-supplemented rats had positive urine sugar. Hypoglycemia precedes the terminal phase of dietary necrotic liver degeneration (Mertz, 1969). Thus, a higher blood glucose level in chromium-supplemented rats may reflect some protection by chromium against hypoglycemia.

6.3.1.1.2 Diabetes — The response to chromium supplementation in diabetes is directly dependent on whether or not the case is complicated by a chromium deficiency (Mertz, 1969). However, no data identify chromium deficiency as a primary causative agent in diabetes even though correlations between chromium metabolism and the diabetic state exist (Mertz, 1974). Insulin-dependent diabetics absorbed two to three times more orally administered chromium chloride than normal human subjects (Doisy et al., 1969, 1971). These diabetics also excreted twice as much chromium chloride as normal control subjects. Maturity-onset diabetics did not show increased absorption and excretion of chromium. Hambidge et al. (cited in Mertz, 1974) suggested that the disturbance in chromium metabolism may be a result rather than a cause of diabetes.

Short-term supplementation of 1.0 mg chromium chloride to seven diabetics for one to seven days had no effect on impaired glucose tolerance

(Glinsmann and Mertz, 1966). Four diabetics were given daily oral doses of 150 to 1000 μg of chromium for 15 to 120 days. Three of these subjects showed significant improvement in oral glucose tolerance. The improvement usually was preceded by a slight impairment of tolerance. Table 6.6 shows the changes in glucose tolerance of one subject during chromium supplementation. Two diabetic outpatients were given the same chromium supplementation; one showed improvement and the other was unaffected. The authors suggested that even though chromium chloride was not particularly useful as a therapeutic agent in diabetes, a certain chromium level may be required for optimal glucose metabolism.

Table 6.6. Effect of chromium on mean glucose tolerance[a]

Chromium supplementation	Days	Number of tests	Mean blood glucose concentration (mg/100 ml)				
			Fasting	Time after glucose load (min)			
				30	60	90	120
None	0-32	10	84	217	229	195	156
60 μg, 3 times a day	33-74	12	85	224	238	209	162
60 μg, 3 times a day	75-119	13	84	210	213	186	141
60 μg, 3 times a day	120-140	5	84	203	201[b]	175	112[b]
None	180-194	1	96	207	290	293	237
60 μg, 3 times a day	195-211	5	83	196	193[b]	175	118[b]
None	256-313	10	87	220	245	224	166
1 mg, 3 times a day	337-340	1	68	148	162	151	96

[a] Subject was maturity-onset diabetic, controlled on diet. Oral glucose tolerance test consisted of constant noon meal and 100 g of glucose.

[b] Mean values significantly different from control ($P < 0.025$).

Source: Adapted from Glinsmann and Mertz, 1966, Table 2, p. 515. Reprinted by permission of the publisher.

Schroeder (1968) reported that glucose metabolism was improved in 4 of 12 diabetic outpatients given up to 1 mg chromic chloride daily for six months. One subject was able to reduce the insulin dose and another ceased taking oral hypoglycemia agents.

The distribution of ^{51}Cr in organs of rats with induced diabetes was not significantly different from that of normal rats (Mathur and Doisy, 1972). However, by inducing diabetes or by feeding high-fat diets, the distribution of ^{51}Cr in the liver fraction was altered. Chromium moved from the nuclear to the microsomal fraction when the rate of hepatic lipogenesis was either normal or elevated. Morgan (1972) found a significant difference in hepatic chromium concentrations between diabetic and normal human subjects. The mean concentration of hepatic chromium was 12.7 μg/g of ash for the normal group and 8.59 μg/g of ash for the diabetic group.

Three hypotheses have been proposed concerning the relationship of chromium to diabetes (Schroeder, 1968):

> (1) Chromium has no role in glucose metabolism in diabetes mellitus. (2) Chromium plays a role in the utilization of glucose by insulin, but absorption of the chloride or acetate is erratic. (3) Chromium deficiency is causal for some part of the disturbed glucose tolerance in some patients with diabetes mellitus, but the proportion cannot be definitely proved until tissue stores are depleted, which has not occurred.

None of these hypotheses have been proven.

6.3.1.1.3 Malnutrition in children — A severe and responsive chromium deficiency in relation to protein-calorie malnutrition exists in several areas of the world (National Academy of Sciences, 1974). Hypoglycemia and impaired glucose tolerance, two symptoms of impaired glucose metabolism, are generally associated with kwashiorkor and marasmus in malnourished children. In a study by Hopkins, Ransome-Kuti, and Majaj (1968), six malnourished infants from the Jordanian hills and six from the Jordan River Valley were given 250 μg chromium chloride. The infants from the hills had severely impaired tolerance (fasting blood glucose levels of 58 mg/100 ml, glucose removal rate of 0.7% increment glucose per minute), whereas tolerance was normal in children from the valley (70 mg/100 ml, 3.8%/min). The children from the valley used drinking water with chromium levels three times that found in water in the hills. Six malnourished Nigerian children with impaired glucose tolerance (1.2%/min) were also given 250 μg chromium chloride. The glucose removal rates of the children from the Jordanian hills improved significantly from 0.6%/min to 2.9%/min (Table 6.7). Lower chromium states apparently occur in parts of Jordan and Nigeria and are associated with impaired glucose tolerance in malnourished children. However, not all cases of malnutrition are complicated with low chromium states and chromium treatment can be expected to improve only those cases which are caused by a low chromium state. In a study of malnourished infants from Turkey, the glucose removal rate significantly improved in 9 of 14 cases after supplementation with 250 μg of chromium chloride (Gurson and Saner, 1971). Similar supplementation caused a significant weight increase in infants with marasmus when compared with a nonsupplemented control group (Gurson and Saner, 1973).

A study in Cairo, Egypt, of 34 infants with kwashiorkor showed that not all cases of impaired glucose tolerance associated with malnutrition are due to chromium deficiency (Carter et al., 1968). The impaired glucose tolerance of the infants in one group improved following consumption of a high-protein, high-calorie diet for one to two weeks. A supplement of 250 μg of chromium as chromic chloride given to another group of children had no effect. Thus, the reversible impaired glucose utilization did not seem to be due to the low chromium diet which the infants habitually received.

Table 6.7. Summary and significance of the effect of chromium on the impaired glucose tolerances of malnourished infants

Subjects	Number of infants	Glucose removal rate (%/min)	Significance of difference
Jordanian infants from hill area with 0.5 ppb chromium in drinking water	10	0.7	$P < 0.001$
Jordanian infants from valley with 1.6 ppb chromium in drinking water	9	3.8	
Jordanian infants			
Initial glucose tolerance test	6	0.6	$P < 0.001$
After chromium treatment	6	2.9	
Nigerian infants			
Initial glucose tolerance test	6	1.2	$P < 0.05$
After chromium treatment	6	2.9	
Nontreated infants			
Initial glucose tolerance test	5	1.9	Not significant
Repeated glucose tolerance test	5	2.1	

Source: Adapted from Hopkins, Ransome-Kuti, and Majaj, 1968, Table V, p. 208. Reprinted by permission of the publisher.

6.3.1.2 Lipid Metabolism — Trivalent chromium increased the synthesis of cholesterol and fatty acids from acetate in rats (Curran, cited in Schroeder, 1968). These early experiments indicated that chromium is essential for lipid metabolism. The effects on lipid metabolism could be the result of the stimulation of glucose metabolism by chromium. In rats, elevated blood cholesterol levels and changes in the major arteries resembling the fatty deposits of arteriosclerosis are signs of chromium deficiency (Schroeder, Mitchener, and Nason, 1971). The addition of 1 ppm chromium to drinking water of male rats significantly lowered serum cholesterol levels as compared to serum cholesterol levels in chromium-deficient rats. Addition of 5 ppm chromium resulted in further reductions in cholesterol levels. Feeding the rats white sugar plus chromium, brown sugar, or raw sugar slowed the rise in serum cholesterol. The addition of 50 ppm cadmium had no consistent effects, whereas 50 ppm molybdenum produced effects similar to those of chromium (Table 6.8).

The relationship between chromium and cholesterol metabolism in rats suggests that human cholesterol levels may rise as a result of chromium deficiencies. Because several other metals cause reductions in cholesterol levels, the action of chromium on circulating cholesterol may not be specific (Mertz, 1969).

A significant difference in the incidence of spontaneous aortic plaques was found between chromium-fed rats and chromium-deficient rats (Schroeder

Table 6.8. Effects of chromium, nickel, molybdenum, and cadmium on fasting serum cnolesterol levels in rats on a starch diet

Metal in basal water	Males		Females	
	Age (days)	Cholesterol level[a] (mg/100 ml)	Age (days)	Cholesterol level[a] (mg/100 ml)
Control 1 (0 ppm chromium)	360	102 ± 4.5		
	510	108 ± 4.4	510	80 ± 7.3
	761	123 ± 8.2	761	95 ± 11.2
5 ppm chromium	360	91 ± 4.8		
	510	77 ± 6.6	510	101 ± 8.2
	761	93 ± 7.6	761	114 ± 9.5
5 ppm cadmium	360	76 ± 4.7		
	510	68 ± 2.8	510	87 ± 9.8
	760	89 ± 8.7	760	113 ± 9.0
Control 2 (1 ppm chromium)	405	111 ± 8.7	405	72 ± 5.3
	657	76 ± 2.9	657	120 ± 9.3
	668	78 ± 2.1	698	116 ± 6.1
	718	92 ± 5.3	718	109 ± 4.0
5 ppm chromium			709	63 ± 4.1
Control 3 (5 ppm chromium)	402	86 ± 3.2	405	72 ± 5.2
	718	67 ± 5.1	726	77 ± 5.2
			480	62 ± 2.7
12 ppm chromium			912	86 ± 3.4
5 ppm nickel and 5 ppm chromium	342	75 ± 2.6	342	75 ± 3.8
	663	49 ± 4.8	663	80 ± 4.7
10 ppm molybdenum and 5 ppm chromium	151	79 ± 4.2	158	77 ± 2.4
	315	76 ± 5.8	315	83 ± 5.4
50 ppm cadmium and 5 ppm chromium	231	74 ± 4.2	331	64 ± 2.4
	576	107 ± 6.1	677	88 ± 2.8
	917	111 ± 12.4	1020	84 ± 5.9

Table 6.8 (continued)

Metal in basal water	Males		Females	
	Age (days)	Cholesterol level[a] (mg/100 ml)	Age (days)	Cholesterol level[a] (mg/100 ml)
Control 4 (5 ppm chromium)	129	46 ± 1.7	129	60 ± 3.4
	476	88 ± 2.4	476	94 ± 3.7
	810	100 ± 7.3	810	85 ± 5.8
50 ppm molybdenum (in doubly deionized water)	135	51 ± 2.2	135	57 ± 1.5
	477	76 ± 4.6	477	74 ± 5.4
	813	76 ± 3.5	813	97 ± 4.2
50 ppm cadmium and 5 ppm chromium	719	99 ± 5.2	719	97 ± 4.3
Control 5 (5 ppm chromium)	90	84 ± 1.9	90	74 ± 4.0
No chromium	115	114 ± 5.0	127	110 ± 2.7
	228	123 ± 10.1	228	91 ± 6.1
	571	78 ± 4.8	571	86 ± 6.0

[a] Mean ± standard error of mean.

Source: Adapted from Schroeder, Mitchener, and Nason, 1971, Table 4, p. 252. Reprinted by permission of the publisher.

and Balassa, 1965). Examination of aortas at the end of the rat's natural life showed the incidence of plaques in chromium-fed rats was 2%, whereas the incidence in the chromium-deficient animals was 19%.

People living in areas of the world where atherosclerosis is mild or virtually absent had higher chromium levels in tissues than people from areas where the disease is endemic (Schroeder, 1968). The greatest difference between foreign and American chromium levels was in the aorta (Schroeder, Nason, and Tipton, 1970). Table 6.9 compares chromium levels in the aortas of subjects who died from arteriosclerotic heart disease to those in subjects who died from other causes. Chromium levels in the aorta were generally lower in patients who died from arteriosclerotic heart disease. Circulating cholesterol levels declined 12.2% in seven of ten patients after five months of chromium supplementation given as 2 mg of the acetate daily (Schroeder, 1968). In patients not receiving chromium supplementation, circulating cholesterol levels decreased only 2.5% to 5.7%. Serum cholesterol levels in three of five diabetics declined to nearly 200 mg/100 ml after they received larger doses of chromium.

Table 6.9. Chromium levels in aortas of subjects dying from arteriosclerotic heart disease, other cardiovascular diseases, and other conditions including accidents

Location	Cause of death	Number of cases[a]	Ash (% dry wt)[b]	Chromium (ppm dry wt)[b]	P[c]
San Francisco	AHD[d]	15(13)[e]	8.3 ± 1.46	0.048 ± 0.009	
	AHD, mild or moderate	3(3)	5.4 ± 0.37	0.028 ± 0.003	
	Accidents	10(2)	5.7 ± 2.46	0.228 ± 0.076	<0.005
United States, nine cities	AHD	13(7)[e]	5.2 ± 0.71	0.052 ± 0.088	
	CVD[f]	15(6)[g]	5.1 ± 0.98	0.196 ± 0.090	
	Accidents	103(13)	5.1 ± 0.38	0.260 ± 0.067	<0.005
Africa	CVD	2	3.8 ± 0.35	0.116 ± 0.026	
	Accidents	5(1)	1.7 ± 0.62	0.072 ± 0.020	
	Other	11(1)	5.4 ± 0.72	0.193 ± 0.025	<0.025
Middle East	CVD	3(1)	4.3 ± 0.40	0.216 ± 0.084	
	Accidents	8(2)	3.7 ± 1.33	0.360 ± 0.143	
	Other	11	4.8 ± 1.31	1.284 ± 0.831	
Far East	ADH	5	4.5 ± 1.03	0.246 ± 0.132	
	CVD	20(3)	2.9 ± 0.39	0.311 ± 0.073	
	Accidents	8	2.7 ± 0.50	0.970 ± 0.532	
	Malignancy	25(1)	3.1 ± 0.26	0.533 ± 0.107	
	Other	21	4.0 ± 0.78	0.438 ± 0.077	

[a] Numbers in parentheses are numbers of cases deficient in aortic chromium.

[b] Mean values are shown.

[c] P is significance of difference between mean for coronary heart disease or cardiovascular disease and other causes of death.

[d] AHD = Arteriosclerotic heart disease with occlusion.

[e] Differs from accident by chi-square analysis, $P < 0.001$

[f] CVD = Cardiovascular and cerebrovascular disease other than AHD.

[g] $P < 0.025$.

Source: Adapted from Schroeder, Nason, and Tipton, 1970, Table 10, p. 132. Reprinted by permission of the publisher.

Even with these data, the effect of chromium on cholesterol levels is difficult to assess. The evidence indirectly points to chromium deficiency as a cause of human atherosclerosis (Schroeder, 1973; Schroeder, Nason, and Tipton, 1970). When large doses of chromium complexes are given orally, elevated cholesterol levels are lowered and glucose metabolism is improved. Human aortas and other arteries with a chromium deficiency may not be capable of oxidizing lipids.

6.3.1.3 Amino Acid Metabolism — Rats fed diets deficient in chromium and protein could not incorporate several amino acids into their heart protein (Roginski and Mertz, 1969). Trivalent chromium supplementation with added insulin significantly improved amino acid incorporation. Glycine, serine, and methionine were the amino acids affected. Lysine and phenylalanine were not affected. Cell transport of an amino acid analog was stimulated to a greater extent by insulin in rats fed low-protein diets with chromium supplementation than in chromium-deficient rats. Chromium may be a cofactor with insulin in two insulin-responsive processes of amino acid metabolism.

6.3.1.4 Eye Lesions — Rats fed a diet containing less than 100 ppb chromium developed visible eye lesions (Roginski and Mertz, 1967). Approximately 10% to 15% of the animals were affected. Final stages of the lesion were opacity of the cornea, dilation of the vessels, and neovascularization of the cornea. Chromium supplementation prevented eye lesions but did not reverse the defect (Mertz, 1969). Corneal opacity in chromium-deficient rats may be a nonspecific reaction to the deficiency.

6.3.2 Nutrition: Chromium Deficiency in Diets

Chromium nutrition in humans depends on the intake of readily absorbed dietary factors (Reinhold, 1975). Total chromium provided daily from a typical institutional diet is about 78 μg (Schroeder, Balassa, and Tipton, 1962). However, daily dietary chromium intake varies from 5 to 115 μg (Mertz, 1969). Drinking water may also provide significant amounts of absorbable chromium. Levander (1975) has reviewed the nutritional aspects of chromium. Hambidge (1974) suggests that chromium nutritional levels are suboptimal in the United States, especially for pregnant women. He feels that supplementation with inorganic chromium would be ineffective in correcting the problem. Hopkins (1971) found, however, that oral trivalent chromium improved glucose tolerance, though GTF supplementation would be better. Chromium deficiencies can be corrected by intake of foods high in glucose tolerance factor (Reinhold, 1975).

Biological values of foods containing available chromium show brewer's yeast to be a good source of usable chromium, followed by meats, grain, and certain seafoods (Mertz, 1974).

Toepfer et al. (1973) also examined the relationship between chromium content of foods and chromium biological activity. Relative biological activity was determined by measuring the carbon dioxide production from glucose oxidation using glucose-1-carbon-14 in the presence of rat epididymal tissue and 100 microunits of insulin. The calculated relative biological activity for various foods is presented in Table 6.10; Tables 8.1 to 8.4 give chromium concentrations in foods. No significant relationship was found between biological activity and total chromium content of foods. A significant relationship existed for chromium extracted with alcohol in meats, fungi, seeds, and seafoods (Figure 6.4).

Chromium-deficient diets are common in the United States because of the amount of refined food which is consumed. Refined fats are generally low in chromium. Milling wheat into refined white flour removes 40% of the chromium. White flour provides approximately 6.6 μg chromium per kilocalorie, whereas whole wheat flour supplies 53 μg/kcal (Schroeder, 1968). Ingestion of refined sugars which contain little or no chromium depletes chromium pools in humans, but this depletion may not occur if the

Table 6.10. Calculated chromium biological values of the edible portion of selected foods as purchased

Food sample	Relative biological value
Yeast, brewer's (dried)	44.88
Pepper, black	10.21
Liver, calf's	4.52
Cheese, American	4.39
Wheat germ	4.05
Bread, whole wheat	3.59
Cornflakes cereal	3.01
Bread, white	2.99
Spaghetti	2.89
Beef round	2.89
Wheat grain	2.96
Butter	2.81
Bread, rye	2.67
Margarine	2.48
Oysters	2.43
Cornmeal, yellow	2.35
Peppers, chili (fresh)	2.27
Wheat bran and middlings	2.21
Vegetarian chicken	2.16
Cornmeal, white	2.09
Shrimp	2.03
Grits	1.97
Lobster	1.95
Mushrooms	1.92
Chicken leg	1.89
Haddock	1.86
Patent flour	1.86
Beer	1.77
Egg white	1.77
Chicken breast	1.75
Vegetarian choplets	1.72
Skimmed milk	1.59

Source: Adapted from Toepfer et al., 1973, Table II, p. 72. Reprinted by permission of the publisher.

sugar contains absorbable chromium. Most of the chromium in raw sugar is removed during refining (Table 6.11). Refined sugar contains 0.5 to 2.5 μg chromium per 100 kcal, whereas raw sugar provides 6.0 to 8.8 μg/100 kcal. Thus, most of the energy in the diet of the average American is obtained from sources that do not supply needed chromium.

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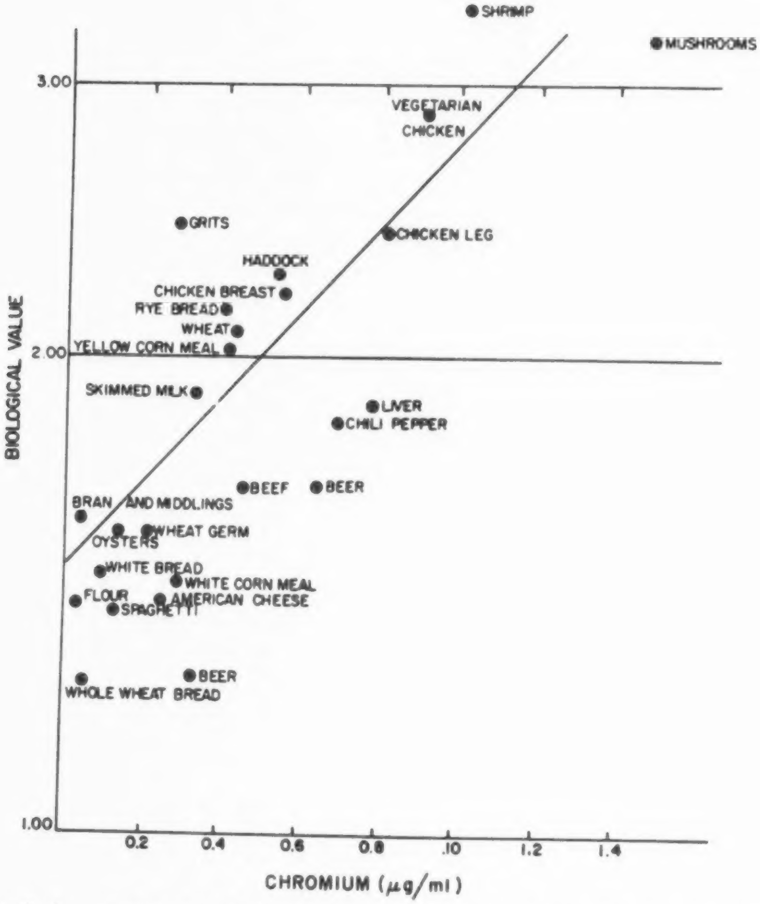

Figure 6.4. Relationship between chromium contents per milliliter of aqueous alcohol extracts of foods and the corresponding biological activities. Source: Toepfer et al., 1973, Figure 1, p. 70. Reprinted by permission of the publisher.

This suboptimal dietary chromium intake may be a cause of the continuous decline of tissue chromium levels with age. Dietary chromium may not be high enough to compensate for the utilization and excretion of chromium, thus causing increasingly lower levels in the body as aging occurs. The high chromium levels in newborns place a stress on chromium concentrations in the mother's body stores (Mertz, 1969). Chromium in the fetus must be supplied from the mother's chromium pool rather than from simple chromium compounds. The mean chromium concentration in hair of parous women was less than a third of that found in hair of nulliparous women (Hambidge and Rodgerson, 1969). Decreasing chromium levels may be a factor in the impairment of glucose tolerance with an increase in the number of offspring (Mertz, 1969).

Table 6.11. Chromium content of sugars

Sugar sample	Chromium (ppm)	Chromium (μg/100 kcal)
Sugar cane, Virgin Islands	0.07	
Sugar cane, Puerto Rico	0.12	
Sugar cane, bark, Puerto Rico	0.15	
Raw sugar, Philippines	0.24	6.0
Raw sugar, Colombia	0.35	8.8
White sugar, United States	0.08	2.0
White sugar, France	0.13	3.3
White sugar, superfine, United States	0.02	0.5
Brown sugar, dark	0.12	3.0
Brown sugar, light	0.06	1.5
Brown sugar, Irish	0.07	1.8
Fructose	0.18	4.5
Glucose	0.03	0.8
Lactose	0.17	4.3
Cerelose	0.17	4.3
Molasses, household	0.11	4.3
Molasses, blackstrap	0.22	8.6
Molasses, refinery	0.27	10.5
Affination syrup	0.75	29.2
Molasses, final	1.21	47.0
Honey, purified	0.29	10.0
Maple syrup	0.18	6.0
Corn syrup	0.15	5.0
Orange juice	0.13	34.0
Grape juice	0.47	94.0

Source: Adapted from Schroeder, 1968, Table VII, p. 240. Reprinted by permission of the publisher.

6.3.3 Toxicity

Chromium, especially trivalent chromium, has low toxicity; amounts needed to produce toxic symptoms are much higher than amounts required to remove symptoms of deficiency. The LD_{50} reported for trivalent chromium injected intravenously into rats was 1 mg chromium per 100 g body weight (Underwood, 1971), an amount more than 10,000 times the dose needed to relieve impairment of glucose tolerance in these same animals. Given orally, trivalent compounds are practically nontoxic due to their insolubility. As reported by Mertz (1969), feeding trivalent chromium to experimental animals at levels of even hundreds of milligrams daily failed to produce toxic symptoms. Schroeder (1968) found only beneficial effects of feeding small amounts of trivalent chromium in lifetime studies with rats and mice. Eaton et al. (1975) studied extractable chromium from printers ink in children's comic magazines. The extraction experiments were designed to simulate absorption after ingestion of paper. Extracted chromium ranged from 100 to 570 ppm and constituted no apparent hazard.

In contrast, symptoms of toxicity have been observed in several species of animals given water containing more than 5 ppm hexavalent chromium (Mertz, 1969). Hexavalent chromium compounds are highly irritating because of the oxidizing power of the hexavalent state. Also, the anions of hexavalent chromium compounds are easily absorbed and penetrate cell membranes easily. However, except for its oxidizing ability, the toxicity of injected hexavalent chromium is not greatly different from that of injected trivalent chromium. Table 6.12 gives the toxicity and uses of some trivalent and hexavalent chromium compounds. Toxic effects of chromates on experimental animals are summarized in Table 6.13; Table 6.14 shows the doses of trivalent chromium which were necessary to produce death.

Chromium toxicity in man is mainly an occupational concern. Industrial exposure to chromium primarily affects the skin, nasal mucous membrane, and lungs (Browning, 1969). Systemic poisoning from chromium, with resulting damage to liver and kidneys, has also been described. Similar lesions have been found in the nonindustrial population after ingestion or external application of chromium compounds.

6.3.3.1 Skin Effects — Workers exposed to chromates in various industries, such as textile dyeing, manufacturing of paint pigments, leather tanning, metal plating, cement masonry, metal and wood polishing, and blueprinting, develop various types of skin injuries (National Academy of Sciences, 1974). Skin reactions to chromium have been classified into two categories: (1) primary irritations with ulcers and nonulcerative contact dermatitis and (2) allergic contact dermatitis with eczematous and noneczematous dermatitis.

Samitz and Katz (1963) demonstrated that hexavalent chromium was reduced by the skin to the trivalent form and then bound to the skin. The chromium reduction may involve divalent sulfur. A correlation was found between the rate of percutaneous absorption and the inactivation of epidermal SH groups (Samitz, 1955).

6.3.3.1.1 Primary dermatoses — Chromium ulcers known as chrome holes are caused by contact with chromate dust and solutions such as chromic acid, sodium or potassium chromate or dichromate, or ammonium dichromate (National Academy of Sciences, 1974). Harmful effects result when chromate comes in contact with a break in the skin (Baetjer, 1956). The incidence of ulcers, which can be high, is related to duration of contact, susceptibility, and hygiene. Chrome holes are generally found on the hands, arms,

Table 6.12. Toxicity and uses of some chromium compounds

Compound	Toxicity	Uses
Ammonium chromic sulfate, $NH_4Cr(SO_4)_2$		As mordant in textile industry; in manufacture of electrolytic chromium metal
Ammonium dichromate(VI), $(NH_4)_2Cr_2O_7$	Causes skin irritation, ulceration, "chrome sores," perforation of nasal septum, pulmonary irritation	As source of pure nitrogen, especially in the laboratory; in pyrotechnics (Vesuvius fire); in lithography and photoengraving; in special mordants, catalysts, and porcelain finishes
Basic cupric chromate, $CuCrO_4Cu(OH)_2$, $CuCrO_4 \cdot 2Cu(OH)_2$, $CuCrO_4 \cdot 3Cu(OH)_2$		In fungicides, seed protectants, and wood preservatives; as mordant in dyeing textiles; in protecting textiles against insects and microorganisms; copper-chromium oxide as a selective hydrogenation catalyst
Chromic acetate, $Cr(C_2H_3O_2)_3$		As a mordant in dyeing; in tanning; in hardening photographic emulsions; to improve light stability and dye affinity of textiles and polymers; in catalyst for polymerization of olefins
Chromic bromide, $CrBr_3$		In catalysts for polymerization of olefins
Chromic carbonate, $Cr_2O_3 \cdot xCO_2 \cdot yH_2O$		In preparation of chromic salts
Chromic chloride, $CrCl_3$	Should be kept tightly closed. MLD (intravenous) in mice 801,000 ppb (see chromium trioxide)	In chromizing; in manufacture of chromium metal and compounds; as catalyst for polymerization of olefins and other organic reactions; as textile mordant; in tanning; in corrosion inhibitors; as waterproofing agent
Chromic fluoride, CrF_3	See chromium trioxide	Hydrates used in printing and dyeing woolens, coloring and hardening marble, mothproofing woolen fabrics, treating silk, polishing metals, and as halogenation catalyst
Chromic formate, $Cr(HCOO)_3$		In printing cotton skeins; in leather tanning and waterproofing
Chromic hydroxide, $Cr(OH)_3$		As pigment such as Guignet's green; in tanning industry, as mordant; as catalyst for organic reactions
Chromic nitrate, $Cr(NO_3)_3$		In preparation of chromium catalyst; in textile printing; as corrosion inhibitor
Chromic oxide, Cr_2O_3		In abrasives; as refractory materials, electric semiconductors; as pigment, particularly in coloring glass; in alloys, printing fabrics, and banknotes; as catalyst for organic and inorganic reactions
Chromic phosphate, $CrPO_4$		As green pigment; in wash primers; in catalysts for dehydrogenation of hydrocarbons and polymerization of olefins
Chromic potassium oxalate, $K_3[Cr(C_2O_4)_3]$		In tanning industry; in dyeing chromate colors on wool
Chromic potassium sulfate, $KCr(SO_4)_2$		As mordant for dyeing fabrics uniformly; in tanning leather, printing calico; for rendering glue and gum insoluble; in manufacture of ink, other chromium salts; for waterproofing fabrics, hardening photographic emulsions
Chromic sulfate, $Cr_2(SO_4)_3$	MLD (intravenous) in mice 247,000 ppb	For insolubilization of gelatin; in catalyst preparation; as mordant in textile industry; in tanning of leather; in chrome plating; in manufacture of Cr, CrO_3, and Cr alloys; to improve dispersibility of vinyl polymers in water; in manufacture of green varnishes, paints, inks, glazes for porcelain
Chromite, $FeCr_2O_4$		As only important commercial ore

Table 6.12 (continued)

Compound	Toxicity	Uses
Chromium, Cr	See chromium trioxide	In manufacture of chrome-steel or chrome-nickel-steel alloys (stainless steel); for greatly increasing resistance and durability of metals; for chrome plating of other metals; man-made Cr-51 isotope used as tracer in various blood diseases and in determination of blood volume (as the chloride or as sodium chromate)
Chromium carbonyl, $Cr(CO)_6$	LD_{50} (intravenous) in mice 100,000 ppb	In catalysts for olefin polymerization and isomerization; as gasoline additive to increase octane number; in preparation of chromous oxide, CrO
Chromium tetrafluoride, CrF_4	A strong irritant	
Chromium trioxide, CrO_3	Dermal contact can cause primary irritation and ulceration as well as allergic eczema. Inhalation can cause nasal irritation, septal perforation. Pulmonary irritation, bronchogenic carcinoma may result from breathing chromate dust. Ingestion causes violent gastrointestinal irritation with vomiting, diarrhea. Renal injury has been reported in experimental animals.	In chromium plating, copper stripping, aluminum anodizing; as corrosion inhibitor; in photography, purifying oils and acetylene, hardening microscopical preparations; medical and veterinary uses: 5% solution as topical antiseptic and astringent, 20% solution as caustic
Chromous acetate, $Cr(C_2H_3O_2)_2$	See chromium trioxide	In preparation of other chromous salts; as O_2 absorber in gas analyses
Chromous bromide, $CrBr_2$		In chromizing
Chromous chloride, $CrCl_2$	See chromium trioxide	In chromizing; in preparation of Cr metal; in catalysts for organic reactions; as O_2 absorbent; in analysis
Chromous fluoride, CrF_2	A strong irritant (see chromium trioxide)	In chromizing; in catalytic cracking of hydrocarbons; as alkylation catalyst; in nuclear reaction fuels
Chromous formate, $Cr(HCOO)_2$		In baths for chromium electroplating; in catalysts for organic reactions
Chromous oxalate, CrC_2O_4		
Chromous oxalate, CrC_2O_4		
Chromous sulfate, $CrSO_4$		As analytical reagent; for absorption of O_2 from gas mixtures; as dehydrohalogenating and reducing agent
Chromyl chloride, CrO_2Cl_2	Burns and blisters the skin; should be handled only in well-ventilated hood	As catalyst for polymerization of olefins; in oxidation of hydrocarbons, in Etard reaction for production of aldehydes and ketones; in preparation of various coordination complexes of chromium
Chromyl fluoride, CrO_2F_2	See chromium trioxide	As fluorination catalyst; to increase olefin-polymer receptivity for dyes
Copper chromium oxide, a mixture of $CuCr_2O_4$ and CuO		Same as cupric chromate(III)
Cupric chromate(III), $CuCr_2O_4$		In fungicides, seed protectants, and wood preservatives; as mordant in dyeing textiles; in protecting textiles against insects and microorganisms; copper chromium oxide as a selective hydrogenation catalyst
Cupric chromate(VI), $CuCrO_4$		Same as cupric chromate(III)
Ferric chromate(VI), $Fe_2(CrO_4)_3$		As pigment for ceramics, glass, and enamels

Table 6.12 (continued)

Compound	Toxicity	Uses
Lead chromate (chrome yellow), $PbCrO_4$	LD_{50} (intraperitoneal) in guinea pigs 400,000 ppb	As pigment in oil and water colors; in printing fabrics, decorating china and porcelain; in chemical analysis of organic substances. Basic lead chromates of colors from brown-yellow to red are used as pigments
Potassium chromate(VI), K_2CrO_4	LD (subcutaneous) in rabbits 12,000 ppb (see chromium trioxide)	Has a limited application in enamels, finishing leather, rustproofing of metals, being replaced by the sodium salt; as a reagent in analytical chemistry
Potassium dichromate(VI), $K_2Cr_2O_7$	Internally, a corrosive poison—30 g reported fatal within 35 min. Industrial contact may result in ulceration of hands, destruction of mucous membranes, and perforation of nasal septum. Chromates have been reported as causing cancer of the lung.	In tanning leather, dyeing, painting, decorating porcelain, printing, photolithography, pigment prints, staining wood, pyrotechnics, safety matches; for bleaching palm oil, wax, and sponges; in waterproofing fabrics; as an oxidizer in the manufacture of organic chemicals; in electric batteries; as a depolarizer for dry cells. As corrosion inhibitor in preference to sodium dichromate where lower solubility is advantageous; medical use: externally as astringent, antiseptic, caustic; veterinary use: as caustic for superficial growths
Sodium chromate(VI), $Na_2CrO_4 \cdot 4H_2O$	LD (subcutaneous) in rabbits 243,000 ppb	In protecting iron against corrosion and rusting
Sodium dichromate(VI), $Na_2Cr_2O_7 \cdot 2H_2O$	Irritant and caustic to skin, mucous membranes (see chromium trioxide)	As oxidizing agent in manufacture of dyes, many other synthetic organic chemicals, inks, etc.; in chrome-tanning of hides; in electric batteries; in bleaching fats, oils, resins, sponges; in refining petroleum; in manufacture of chromic acid, other chromates, and chrome pigments; in corrosion inhibitors, corrosion-inhibiting paints; in many metal treatments; in electroengraving of copper; as mordant in dyeing; for hardening gelatin; for defoliation of cotton plants and other plants and shrubs; medical use: in solution as antiseptic, astringent, caustic

Source: Adapted from Sullivan, 1969, Table 7, pp. 49-58.

and feet. The first sign of chrome ulcers is the appearance of papules which change to pustules. These pustules become deep ulcers with thickened, indurated, undermined tissue around the ulcer. Ulcers, if neglected, penetrate to the bone, are difficult to heal, and persist for long periods of time.

Chrome holes may be caused by the oxidizing properties of hexavalent chromium (Samitz, Shrager, and Katz, 1962), which causes denaturation of skin proteins. This corrosive action of the chromate ion is independent of its sensitizing properties. The toxic effects of hexavalent chromium can be prevented by reducing chromium to the trivalent form.

In a study of workers from a chromate manufacturing plant, Edmundson (1951) found that of 285 workers, 60.5% had chrome ulcers or scars. The distribution of ulcers and scars was: hands, 31% to 46%; arms, 19.5%; ankles and feet, 10.1%; legs, 6.0%; back, 4.1%; knees, 3.6%; thighs, 3.3%;

Table 6.13. Animal exposures to chromates

Species	Type of exposure	Material	Average dose or concentration	Duration	Effect
Rabbits and cats	Inhalation	Chromates	1-50 mg/m^3	14 hr/day 1-8 months	Pathological changes in lungs
Rabbits	Inhalation	Dichromates	11-23 mg/m^3	2-3 hr for 5 days	No effect
Cats	Inhalation	Dichromate	11-23 mg/m^3	2-3 hr for 5 days	Bronchitis, pneumonia
Mice	Inhalation	Mixed dust containing chromates	1.5 mg/m^3 as CrO_3	4 hr/day, 5 days/week for 1 year	No harmful effects
Mice	Inhalation	Mixed dust containing chromates	16-27 mg/m^3 as CrO_3	½ hr/day intermittently	Fatal to some strains
Mice	Inhalation	Mixed dust containing chromates	7 mg/m^3 as CrO_3	37 hr over 10 days	Fatal
Rats	Inhalation	Mixed dust containing chromates	7 mg/m^3 as CrO_3	37 hr over 10 days	Barely tolerated
Rabbits and guinea pigs	Inhalation	Mixed dust containing chromates	5 mg/m^3 as CrO_3	4 hr/day, 5 days/week for 1 year	No marked effects
Rats	Ingestion	Potassium chromate added to drinking water	500 μg/g	Daily	Maximum nontoxic level
Mature rats and mice	Ingestion	Zinc chromate in feed	10 mg/g	Daily	Maximum nontoxic level
Young rats	Ingestion	Zinc chromate in feed	1.2 mg/g	Daily	Maximum nontoxic level
Young rats	Ingestion	Potassium chromate in feed	1.2 mg/g	Daily	Maximum nontoxic level
Dogs, cats and rabbits	Ingestion	Mono- or dichromates	1.9-5.5 mg chromium per kilogram body wt	29-685 days	No harmful effects
Dogs	Ingestion	Potassium dichromate	2.8-5.7 g	Daily	Fatal in 3 months

Table 6.13 (continued)

Species	Type of exposure	Material	Average dose or concentration	Duration	Effect
Dogs	Stomach tube	Potassium dichromate	2.8-5.7 g		Rapidly fatal
Monkeys	Subcutaneous	Potassium dichromate	20-700 mg of 2% solution		Fatal
Dog	Subcutaneous	Potassium dichromate	594 mg		Rapidly fatal
Guinea pigs	Subcutaneous	Potassium dichromate	10 mg		Lethal
Rabbits	Subcutaneous	Potassium dichromate	1.5 g of 1% solution per kilogram body wt		80% fatal
Rabbits	Subcutaneous	Potassium dichromate	20 mg		Lethal
Rabbits	Subcutaneous	Potassium dichromate	0.5-1.0 g of 0.5% solution per kilogram body wt		Nephritis
Rabbits and guinea pigs	Subcutaneous or intravenous	Sodium chromate	162-486 mg		Rapid death
Mice	Intravenous	Zinc chromate	100 μg/month	10 months	Tolerated
Mice	Intravenous	Zinc chromate	750 μg	One dose	Fatal
Mice	Intravenous	Barium chromate	2.5 mg	Nine doses at 6-week intervals	Tolerated
Rabbits	Intravenous	Potassium dichromate	0.7 g of 2% solution per kilogram body wt		Fatal
Dogs	Intravenous	Potassium chromate	10 g		Fatal
Dogs	Intravenous	Potassium chromate	23 mg		Survived
Dog	Intravenous	Potassium dichromate	594 mg		Rapidly fatal
Dog	Intravenous	Potassium dichromate	3 mg/100 ml blood	Two doses	Marked kidney damage

Source: Adapted from Sullivan, 1969, Table 9, pp. 60-63.

Table 6.14. Fatal doses of trivalent chromium in animals

Animal	Route[a]	Material	Chromium dose (g/kg)	Effect
Dog	SC	Chromic chloride	0.8	Fatal
Rabbit	SC	Chromic chloride	0.52	Fatal
Rat	IV	Chrome alum	0.01-0.018	LD_{50}
		Chromium-hexaurea chloride		
Mouse	IV	Chromic chloride	0.8	MLD
	IV	Chromic acetate	2.29	MLD
	IV	Chromic chloride	0.4	MLD
	IV	Cr(III)	0.25-2.3	MLD
	IV	Chromic sulfate	0.085	MLD
	IV	Chromium carbonyl	0.03	LD_{50}

[a] SC = subcutaneous; IV = intravenous.

Source: Adapted from National Academy of Sciences, 1974, Table 8-3, p. 79.

abdomen, 3.0%; face, 1.9%; neck, 1.6%; and chest, 0.6%. Contact with alkali chromates or chromic acid, the number of abrasions as a result of job conditions or worker's carelessness, and inadequate care given to the abrasions were factors in the occurrence of the ulcers. Exposure to chromic acid or its alkali salts did not sensitize workers to potassium dichromate.

The incidence of chrome ulcers among chromate workers has decreased over the years. More efficient ventilating systems reduce the concentration of chromate mist in the air and thus reduce the amount of contact with chromium by workers. Henning (1972) reported that the entrance of chromic acid mist into workroom air can be prevented by using lip exhaust ventilation at the chromic acid bath and chemical suppressants which reduce surface tension or by building a layer of foam to act as a physical barrier to the mist. Covering skin areas where abrasions appear prevents chromium penetration. Samitz, Scheiner, and Katz (1968) found ascorbic acid to be an effective antichromium agent. The mechanism for hexavalent chromium inactivation by ascorbic acid involved reduction to trivalent chromium followed by complex formation of the trivalent form. Ten percent aqueous ascorbic acid applied to abrasions treated with potassium dichromate significantly reduced healing time of chromate ulcers in guinea pigs

(Pirozzi, Gross, and Samitz, 1968). If more time elapsed before the application of ascorbic acid, more time was required for healing. Even after a 30-min delay, however, healing time was reduced. Ascorbic acid acted by reducing the hexavalent chromium salt to the trivalent state. These results agree with the findings of Samitz, Shrager, and Katz (1962).

6.3.3.1.2 Contact dermatitis and allergic responses — A diffuse dermatitis results from skin contact with low concentrations of hexavalent chromium compounds. Eczematoid dermatitis is considered an allergic reaction to chromates; sensitization may take place within a few days or after several years of exposure (Baetjer, 1956).

Even though dermatitis is often caused by hexavalent chromium, it is just as prevalent with trivalent compounds (Hamilton and Hardy, 1974). Mali, Malten, and Van Neer (1966) reported, however, that a higher concentration of trivalent chromium was needed to cause an allergic reaction. A level of at least 20 times that of hexavalent chromium was needed for an epicuticular reaction and 50 times as much for an intracutaneous reaction. Individual chromium sensitivities also differ between hexavalent and trivalent compounds. Those persons slightly sensitive to dichromate may not react to trivalent chromium. Samitz and Gross (1961) tattooed guinea pigs with both trivalent and hexavalent chromium compounds. They reported no significant difference in the absorption of these compounds. As a result of other experiments with guinea pigs, Scheiner and Katz (1973) proposed that the binding of chromium by protein depends on the concentration of free trivalent chromium ions in solution. In the presence of strong ligands such as oxalate, little chromium is bound because most of it is complexed and is not available to the protein. With a weak ligand, a higher concentration of free ions allows more binding. The presence of strong ligands may inhibit formation of the complete antigen with respect to eliciting allergic reactions.

Cases of chromatic dermatitis have been reported in several industries. Morris (1955) reported dermatitis in persons making and using chrome glue manufactured from leather trimmings which contained chromium. Levin et al. (cited in National Academy of Sciences, 1974) showed that dermatitis in lithographers was principally caused by chromium compounds. Eczematous contact dermatitis was prevented by workers soaking their hands and forearms in 10% ascorbic acid solution (Samitz and Shrager, 1966).

An outbreak of dermatitis developed in 60 of 250 automobile-factory workers engaged in wet-sanding primer painting (Engel and Calnan, 1963). The latent period before dermatitis appeared was four to six months. Patch tests showed that zinc chromate was the causal agent. Symptoms varied from erythema to dyshidrotic and exudative eczema. In another study of 230 automobile assemblers, potassium dichromate was the most common sensitizing agent out of nine common sensitizing substances tested. Positive reactions occurred in 36% of the workers (Newhouse, 1963). Incidence of chromium sensitivity was four times greater among assemblers than among those with other jobs. The chromate source was a dip used in chromium plating and zinc coating.

Shelly (1964) found that inhalation of chromium fumes generated from acetylene welding rods caused a severe eczematous eruption on the palms of a chromium-sensitive patient. Some welding rods contain up to 18% chromium. Fregert and Ovrum (1963) found that close exposure to chromium vaporized from welding rods elicited contact dermatitis on the face of a chromium-sensitive welder.

Four patients with shoe-leather dermatitis reacted positively to patch tests with 0.2% trivalent basic chromic sulfate, which is the material used to tan shoe leather (Morris, 1958). Leather workers with chromium dermatitis reacted to the trivalent material; a diesel engine inspector exposed to hexavalent chromium reacted to the hexavalent material but not to trivalent chromium. The author concluded that shoe-leather dermatitis could be caused by sensitization to the basic chromic sulfate leached from the shoe by the patient's sweat.

Samitz and Gross (1960) and Samitz, Katz, and Gross (1960) proved that human sweat could extract both trivalent and hexavalent chromium compounds from shoe leather. They theorized that hexavalent compounds were more likely to cause sensitization because they have a higher sensitizing index and are more diffusible. The hexavalent chromium may either have been a contaminant from the tanning process or have been oxidized from trivalent chromium by some readily reducible substance. In another study, Samitz and Gross (1961) found no evidence for cross-sensitization between hexavalent and trivalent chromium compounds. An anti-chrome agent was developed to reduce hexavalent to trivalent chromium without harming the skin (Samitz, Gross, and Katz, 1962). The reagent contained sodium pyrosulfite to reduce the chromium and tartaric acid to chelate the trivalent chromium formed. The application of an ointment containing these compounds effectively blocked reactions in two chromate-sensitive patients 15 and 30 min after 0.25% potassium dichromate was applied.

Fregert (1961) reported that the hexavalent chromium content in unburnt match heads was as high as 1.7%. The chromate caused allergic eczematous contact dermatitis in sensitive people because the match heads partly dissolved when held by moist fingers. The pockets of many of these people contained chromate from matches. The eczema cleared up in some people when contact with the matches was eliminated.

Studies by Mali, Van Kooten, and Van Neer (1963) to investigate the capacity of chromium salts to bind with serum and dermal proteins, chromium diffusion, membrane potentials, reduction of dichromate by skin components, permeation of chromium salts through living skin, chromium sensitivity of patients, and animal sensitization lead to several conclusions about behavior of chromium compounds in the skin. Trivalent chromium salts have a strong affinity for the epithelial and dermal structures, but affinity of hexavalent compounds is weak. Because trivalent chromium salts possess this strong affinity and tend to form large complexes, their diffusibility through tissues is reduced and, therefore, their ability to induce sensitization is low. However, small amounts of the trivalent compound formed by the interaction between dichromate and tissues would be predisposed to form a hapten-protein complex as the first step in sensitization. The possible in vitro reduction of dichromate and the fact that guinea pigs injected with trivalent chromium were sensitized to hexavalent chromium point to the formation of a chromium-protein complex as the first step in the sensitization process.

Allergic reactions in several patients with green tattoos have been reported (Loewenthal, 1960). There appeared to be an association of dermal granulomatous and epidermal eczematous allergic reactions. These reactions may be the result of contamination of the trivalent chromium used in the tattoos with some hexavalent chromium.

In sensitization studies, Fregert and Rorsman (1964) found that humans allergic to hexavalent chromium are usually also allergic to trivalent chromium. Patch testing with trivalent chromium showed that a response was produced if the concentration of the test material was high enough. Basophil leukocytes were increased in the inflammatory exudates produced by both trivalent and hexavalent chromium. In a later study, hexavalent compounds elicited stronger allergic reactions than trivalent compounds; the intensity of the reactions to trivalent chromium compounds depended on the anions (Fregert and Rorsman, 1966).

In guinea pigs, sensitization, once induced, was long-lived (Gross, Katz, and Samitz, 1968). Cross-sensitization between hexavalent and trivalent chromium salts occurred; potassium dichromate was the most effective sensitizer tested. The trivalent chromium ion appeared to be responsible for sensitization. Sensitization differences were a result of the availability of the chromium to form a complete antigen by conjugation with a carrier protein. The subcutaneous injection of relatively large doses of potassium dichromate (10 mg in Freund's complete adjuvant) to guinea pigs temporarily inhibited sensitization (Jansen and Berrens, 1968). The guinea pigs gradually returned to the original sensitivity level as shown by allergic responses to various chromium compounds. Schneeberger and Forck (1974) produced contact sensitization and allergic responses in guinea pigs with both hexavalent and trivalent chromium salts. The sensitization capabilities of the trivalent complexes were proportional to the release of chromium from the complex. In chromium-sensitized guinea pigs, serum albumin was an active carrier of chromium (Katz et al., 1974). Chromium-globulin complexes were not directly involved in the allergic response mechanism.

6.3.3.2 Respiratory Effects

6.3.3.2.1 Perforation of the nasal septum — A common effect of chromate dust or chromic acid mist inhalation is ulceration and perforation of the nasal septum (Baetjer, 1956). The incidence of this condition varies with degree of exposure — the greater the exposure, the higher the incidence rate. The perforation is limited to the cartilage of the septum; the mucous membrane covering this area is less vascular than the membrane lining the rest of the nasal passage and is easily destroyed (National Academy of Sciences, 1974). Blood supply to the cartilage is stopped and necrosis occurs. The first symptom is a hyperemic reaction with sneezing, swelling, and secretion (Baetjer, 1956). A mucous crust forms about the perforation and is later expelled. Some irritation may be noticed but there is practically no pain. The perforation is not disabling and is sometimes unnoticed by the workers. Nasal irritation seems to occur at atmospheric concentrations of 0.1 mg chromic acid per cubic meter and may occur at even lower levels (U.S. Department of Health, Education, and Welfare, 1973).

In a survey of various electroplating factories, Gomes (1972) found 86.8% of the workers exposed to chromic acid mist had symptoms ranging from scarring to perforation of the nasal septum. Perforated nasal septums were present in 24%; 38.4% had ulcerations of the septum. The threshold limit of exposure (0.1 mg/m^3) was exceeded by more than 50% of the workers; in one case, the atmospheric concentration was 1.40 mg/m^3.

Kleinfeld and Rosso (1965) examined nasal injuries in nine workers in a chrome-plating plant. Table 6.15 summarizes their findings. Air sample analyses showed chromium concentrations of 0.18 to 1.4 mg/m^3. The effect of time at a fixed chromium concentration was not reported. Ulceration of the septum was found in seven workers and four showed perforation of the septum. Chromic acid was the responsible agent.

Table 6.15. Nasal injuries in a chromium-plating plant

Case	Age (years)	Duration of exposure (months)	Findings
1	30	6	Perforated septum
2	19	2	Perforated septum
3	19	12	Perforated septum
4	18	9	Perforated septum
5	47	10	Ulcerated septum
6	45	6	Ulcerated septum
7	23	1	Ulcerated septum
8	20	0.5	Moderate injection of septum and turbinates
9	48	9	Moderate injection of septum

Source: Adapted from Kleinfeld and Rosso, 1965, Table I, p. 242. Reprinted by permission of the publisher.

Workers who inhaled a mist from 5% chromic acid solution were affected in varying degrees (Zvaifler, 1944). In 50% to 60% of the cases, only the anterior part of the septum showed a superficial ulceration. About 35% had deeper ulcerations, usually of the anterior part of the inferior turbinate. Symptoms similar to those of atrophic rhinitis developed in 5% to 10% of the workers. The injury to the nasal mucosa caused by exposure to the anodizing mist differed from that of chrome plating; the involvement, while widespread, did not include perforation. In another study, Edmundson (1951) found 61.4% of the chrome workers examined had perforated septa.

Bloomfield and Blum (cited in National Academy of Sciences, 1974) examined workers in six U.S. chrome-plating plants. Their findings are reported in Table 6.16. They concluded that continuous daily exposure to chromic acid concentrations greater than 0.1 mg/m^3 caused injury to nasal tissue. Concentrations below 0.1 mg/m^3 generally have not been studied; therefore, their effects are not known.

6.3.3.2.2 Cancer of the respiratory tract — Increased incidence of lung cancer is a long-term effect of exposure to hexavalent chromium from the manufacturing of dichromate from chromite ore (National Academy of Sciences, 1974). The incidence of cancer at other body sites is not increased. Respiratory cancer usually occurs only after several years of exposure and may not appear until long after exposure has ended. The dose-response relationship between chromium and respiratory cancer is not known. The chromium concentration in factories usually has not been measured. Even if the concentration was measured at the time of cancer diagnosis, it was not necessarily the same as that at the time of exposure. It is not known which specific compounds in chromate manufacturing are responsible for the increased incidence of cancer (Baetjer, 1956). Most cases of cancer of the respiratory tract have been bronchogenic carcinomas. A few cases of cancer have occurred in the upper respiratory tract, including the sinus, pharynx, and oral region.

Bidstrup (1951) examined chest x rays of 724 workers in an English chromate-producing industry and found one pulmonary carcinoma. A later study of chromate workers in three chromate-producing factories showed a significant increase in mortality from carcinoma of the lung above that of the general population (Bidstrup and Case, 1956). Only 3.3 deaths from lung cancer were expected, but 12 deaths were reported. The mean latent period was calculated to be 21 years with a standard deviation of 10 years. The authors concluded that carcinoma of the lung was an occupational hazard of the chromate-producing industry.

In a survey of pulmonary carcinoma in chromate workers by Baetjer (1950*a*), the duration of exposure varied greatly. Variations in the latent period may have been related to the degree of exposure. In most cases, the onset of illness occurred while the men were employed at the chromate plant. Atmospheric chromate concentrations were not known. Pathological examination showed that the tumors usually arose from the main bronchi; oat, squamous, undifferentiated epithelial, or anaplastic tumors were identified. Baetjer (1950*b*) compared the number of chromate workers among patients with lung cancer and the number of chromate workers among other

Table 6.16. Clinical findings in workers employed in chromium-plating plants

Case	Occupation	Time employed in chromium-plating room (months)	Time over tank (hr/day)	Approximate CrO_3 exposure (mg/cu m)	Perforated septum[a]	Ulcerated septum[a]	Inflamed mucosa[a]	Nosebleed	Chrome holes
1	Chromium plater	6	4	1.5	++	-	++	Yes	Yes
2	Chromium plater	20	4	2.8	++	-	+	Yes	Yes
3	Foreman plater	7	2	2.5	-	++	++	Yes	No
4	Foreman plater	8.5	3	2.5	-	++	++	Yes	No
5	Chromium plater	3.5	4	5.6	-	++	++	Yes	Yes
6	Chromium plater	0.75	7	0.12	-	-	++	Yes	Yes
7	Chromium plater	0.25	7	0.12	-	-	++	Yes	No
8	Chromium plater	7	7	0.12	-	-	++	Yes	No
9	Chromium plater	3	7	0.12	-	-	++	No	Yes
10	Chromium plater	36	4	0.2	-	-	++	No	No
11	Chromium plater	5	6	0.12	-	-	+	Yes	Yes
12	Chromium plater	0.75	6	0.12	-	-	+	No	No
13	Chromium plater[b]	12	4	2.8	-	-	-	No	No
14	Chromium plater	0.67	2	2.8	-	-	-	No	No
15	Nickel plater[c]	1.5	0		-	+	+	Yes	No
16	Racker	8	0		+	-	+	Yes	No
17	Racker	0.75	0		-	-	+	No	No
18	Racker	0.75	0		-	-	+	No	No
19	Wiper	1.5	0		-	-	+	No	No
20	Foreman[d]	0	0	0	-	-	+	No	No
21	Foreman[d]	0	0	0	-	-	+	No	No
22	Clerk[d]	0	0	0	-	-	-	No	No
23	Inspector[d]	0	0	0	-	-	+	No	No

[a] ++, marked; +, slight; -, negative.
[b] Used vaseline in nose.
[c] Cyanide burns.
[d] Worked in other departments of factory.

Source: Adapted from Bloomfield and Blum as reported in National Academy of Sciences, 1974, Table 7-1, p. 44.

hospitalized groups selected as controls. The percentage of lung cancer patients who had been exposed to chromates was significantly higher than would be expected on the basis of the control hospitalized groups.

In an epidemiologic study of lung cancer deaths among workers of a U.S. chromate plant, Mancuso and Hueper (1951) reported a lung cancer death rate which was approximately 15 times that of the general population living in the county in which the plant was located. The latent period was 10.6 years. The authors suggested that insoluble chromium compounds may produce lung cancer because these compounds are retained in the lung over long periods of time. Brinton, Frasier, and Koven (1952) also reported a higher frequency of respiratory cancer among chromate workers than among workers in other industries. Langard and Norseth (1975) found an increased incidence of bronchial carcinoma among workers in a factory producing zinc chromate. The risk ratio for exposed workers was approximately 38. All workers had been exposed mainly to zinc chromate dust; the exposure levels of the workers who developed bronchial cancers probably were from 0.5 to 1.5 mg chromium per cubic meter for six to nine years.

Attempts to produce lung tumors with chromium by inhalation have been unsuccessful in experimental animals. Baetjer et al. (1959) exposed mice and rats to various chromium compounds. Animals were exposed by inhalation of air from a chromate-producing plant where the concentration of chromium trioxide was 1 to 3 mg/m^3. Other animals were given intrapleural or intratracheal injections of chromium trioxide. No bronchogenic carcinomas were found in any of the animals. Intratracheal injection of zinc chromate produced an epithelization of the alveoli. Nettesheim et al. (1970) did not affect the lung tumor incidence in mice exposed daily for 5½ hr/day, 5 days/week to an aerosol of chromium oxide dust at a concentration of 25 mg/m^3. Autopsy and histopathological examinations were performed at 6, 12, and 18 months. Steffee and Baetjer (1965) were unable to produce malignant tumors in rabbits, guinea pigs, rats, and mice by inhalation and/or intratracheal injection of various chromium compounds under conditions simulating the exposures in old chromate-refining plants. The effects caused by the chromium compounds are summarized in Table 6.17.

Other experimental data have shown that sarcomas can be produced locally by injection and by implantation of various chromium compounds, but no dose-response relationship is available from the data. Payne (1960*a*) exposed mice to calcium chromate, sintered calcium chromate, and sintered chromium trioxide (10 mg of chromium compound) by implantation into the thigh muscle and subcutaneous injection. After 7 to 13 months, spindle cell or fibrosarcomatous tumors occurred at the site of implantation of calcium chromate or sintered calcium chromate. No tumors were produced by subcutaneously injected sintered chromium trioxide or sintered calcium chromate. A summary of results from an experiment with rats by Hueper and Payne (1959) is presented in Table 6.18. Calcium chromate, sintered calcium chromate, sintered chromium trioxide, and barium chromate (25 mg of chromium compound) were implanted intramuscularly and intrapleurally. The cancers produced were mainly sarcomas which occurred at the site of implantation. This effect was related to the degree of solubility of these compounds in an aqueous medium. Barium chromate with low solubility did

Table 6.17. Microscopic pulmonary findings in rabbits, guinea pigs, rats, and mice after inhalation and intratracheal injections of chromate material

Method of exposure	Total number of animals	Edema	Hyperemia	Hemorrhage	Emphysema	Atelectasis	Bronchiectasis	Abscesses	Bronchopneumonia	Interstitial pneumonitis	Alveolar & interstitial inflammation	Alveolar hyperplasia	Interstitial fibrosis	Giant cells	Granulomas	Alveologenic adenomas	Lymphosarcoma
	Number of animals exhibiting various symptoms																
							Rabbits										
Inhalation																	
Mixed dust	8	3	5	4	0	6	0	0	3	1	4	1	0	1	1	0	0
Controls	5	3	1	1	0	4	0	1	1	0	1	0	0	0	0	0	0
Intratracheal experimental																	
Dry mixed dust	10	6	3	2	0	6	0	3	4	2	0	2	1	0	1	0	0
Zinc chromate	7	4	3	4	1	0	0	3	2	1	4	6	0	0	2	0	0
Lead chromate	7	7	4	4	0	7	0	1	3	0	3	1	0	0	0	0	0
Residue	7	3	2	3	0	7	0	2	3	1	2	2	0	0	2	0	0
Controls																	
Dry portland cement	2	1	0	0	0	2	0	1	0	0	0	0	1	1	0	0	0
Saline	5	4	2	2	0	3	0	1	2	1	0	0	0	0	0	0	0
No injection	2	0	1	1	0	1	0	1	0	0	1	0	0	0	0	0	0
							Guinea pigs										
Inhalation																	
Mixed dust	50	13	14	16	32	34	0	7	18	4	23	13	6	3	1	3	1
Controls	44	22	14	10	28	32	0	4	9	6	6	0	0	3	0	0	1
Intratracheal experimental																	
Mixed dust	19	4	7	3	10	9	8	0	4	1	11	2	0	2	1	0	0
Zinc chromate	21	7	6	6	13	8	0	7	14	5	12	13	5	2	4	1	0
Lead chromate	13	1	4	3	6	7	0	3	7	1	6	2	1	1	2	0	0
Residue	19	4	2	7	5	9	1	6	8	5	9	1	0	2	3	0	1
Controls																	
Dry portland cement	8	1	2	2	3	4	0	1	2	0	1	0	1	1	0	0	0
Wet portland cement	7	0	1	2	2	4	0	2	2	0	3	2	1	0	0	0	0

Table 6.17 (continued)

Method of exposure	Number of animals exhibiting various symptoms																
	Total number of animals	Edema	Hyperemia	Hemorrhage	Emphysema	Atelectasis	Bronchiectasis	Abscesses	Bronchopneumonia	Interstitial pneumonitis	Alveolar & interstitial inflammation	Alveolar hyperplasia	Interstitial fibrosis	Giant cells	Granulomas	Alveologenic adenomas	Lymphosarcoma
Rats																	
Inhalation																	
Mixed dust	78	16	15	19	37	37	24	40	57	5	22	5	0	25	12	3	4
Control	75	33	14	17	44	49	41	17	35	5	12	2	0	4	1	2	4
Intratracheal																	
Chromate, then virus	32	13	14	8	24	28	19	15	11	8	3	7	1	4	1	0	1
Virus, then chromate	35	13	24	12	32	33	17	11	17	3	1	8	3	3	0	2	1
Virus only	38	6	21	13	23	22	11	8	13	11	2	2	0	1	0	1	3
Chromate only	38	13	19	9	32	28	21	14	23	2	4	8	0	1	0	0	2
Mice																	
Intratracheal																	
Zinc chromate early[a]	11	4	2	7	0	5	0	0	0	0	6	4	0	0	0	0	0
Zinc chromate	62	20	22	24	12	21	16	2	8	18	45	28	2	0	1	31	2
Zinc carbonate early[a]	7	2	1	3	0	0	0	0	1	1	1	0	0	0	0	0	0
Zinc carbonate	12	2	2	7	2	6	0	0	3	1	1	1	0	0	0	3	0
No injections	18	5	9	6	2	7	4	1	10	1	2	2	0	0	0	7	2

[a] The groups designated "early" include those animals that died or were killed within the first 6 months. The first tumors appeared at 6½ months in the zinc chromate and zinc carbonate groups.

Source: Adapted from Steffee and Baetjer, 1965, Table 1, p. 67. Reprinted by permission of the publisher.

Table 6.18. Death distribution and tumors observed in rats at site of implants of chromium compounds and of sheep fat[a]

Chromium compound	Site of implant	Deaths in periods of months after administration of material								Duration of exposure (months)	Number dead	No tumor at site	Percent of dead with tumors
		0-3		4-6		7-9		10-12					
		With tumor	No tumor	With tumor	No tumor	With tumor	No tumor	With tumor	No tumor				
$CaCrO_4$	Thigh	0	1	3	4	5	0	0	0	13	13	8	62
	Pleural	0	3	7	1	13	5	1	5	12	35	21	60
Sintered $CaCrO_4$	Thigh	0	1	6	2	2	1	0	2	14	14	8	57
	Pleural	0	2	3	4	13	2	1	1	14	26	17	65
Sintered CrO_3	Thigh	0	0	4	3	8	0	3	1	12	19	15	79
	Pleural	0	1	2	1	8	2	4	2	12	20	14	70
$BaCrO_4$	Thigh	0	2	0	1	0	1	0	1	12	5	0	0
	Pleural	0	0	0	3	0	1	0	1	12	5	0	0
Sheep fat	Thigh	0	1	0	1	0	1	0	3	12	6	0	0
	Pleural	0	0	0	1	0	3	0	1	12	5	0	0

[a] Number of rats at beginning of experiment: 35 (20 male and 15 female) for each material at each site.

Source: Adapted from Hueper and Payne, 1959, Table I, p. 275. Reprinted by permission of the publisher.

not produce tumors in rats during the same period of time. Thus, chromium was capable of producing carcinomas of the lung and sarcomas of the soft tissues of the mediastinum and thigh. Laskin, Kuschner, and Drew (1970) used intrabronchial pellets in rats to determine the carcinogenic effect of ore-roast residue, calcium chromate, chromic oxide, and chromium trioxide. Lung cancers were produced that closely duplicated human lung pathology (Table 6.19). The mean cancer induction time was 540 days. All carcinomas occurred at the site of pellet implantation.

Table 6.19. Carcinomas produced with chromium compounds in rats

Material	Number of animals	Squamous cell carcinoma	Adeno-carcinoma	Hepatocell carcinoma
Process residue	100	1		1
Calcium chromate	100	6	2	
Chromic chromate	100			1
Chromic oxide	98			
Chromic trioxide	100			2
Cholesterol control	24			

Source: Adapted from Laskin, Kuschner, and Drew, 1970, Table 5, p. 334.

Zinc chromate, widely used as an anticorrosive paint pigment, may also possess carcinogenic properties since it is slightly more soluble than the carcinogenic strontium chromate. Chromite ore roasts implanted into the pleural cavity and into the thigh muscle of rats produced squamous cell carcinomas along with sarcomas of the lung (Hueper, 1958). Fibrosarcomas were found in the thighs of the rats. Further studies by Payne (1960*b*) in which roasted chromite ore fractions (10 mg) were injected subcutaneously into rats indicated that intermediate products in the production of chromium chemicals and the discarded residue may be harmful. Implantation of these fractions produced sarcomas in 4 of 70 rats. Calcium chromate injected intramuscularly into rats produced spindle cell and pleomorphic cell sarcomas in 75% of the test rats (Roe and Carter, 1969). Sarcomas were produced at the injection site and were locally invasive. Schoental (1975) hypothesized that the mechanism of action involved oxidation of glyceral and fatty acids by the hexavalent chromium to yield carcinogenic aldehydes and epoxyaldehydes. However, proof is lacking.

Hueper and Payne (1962) found in experiments with rats that both hexavalent and trivalent chromium possessed carcinogenic properties. Sodium dichromate (2 mg) injected intrapleurally produced an adenocarcinoma of the right lung. Chromic acetate (25 mg), a trivalent chromium compound, induced only a weak carcinogenic response from muscular tissue. One anaplastic spindle cell sarcoma was found at the site of implantation.

6.3.3.2.3 Other respiratory effects — Dusts and mists which contain low concentrations of hexavalent chromium irritate the respiratory system and can cause sneezing, rhinorrhea, redness of the throat, and general bronchospasm (National Academy of Sciences, 1974). Higher chromium concentrations may cause coughs, headaches, dyspnea, and substernal pain.

In two cases where large amounts of chromic acid mist were inhaled, the nasal mucosa was only mildly hyperemic, but deep pulmonary structures were severely damaged (Meyers, 1950). Weight loss, coughing, chest pain, and pleural effusion were present in both cases. Six months after exposure both patients still experienced sharp, burning chest pains on deep inspiration. Williams (1969) reported two asthma cases which were related to chromium inhalation. One patient was exposed to chromic acid mist and the other to zinc chromate in a primer paint. The asthmatic conditions subsided when the patients were gradually removed from contact with the chromium source.

6.3.3.3 Systemic Effects — Although explicit proof of systemic poisoning due to occupational exposure to chromium compounds is lacking, a relationship between the two may exist. A study of several workers in a chromium-plating plant (Pascale et al., 1952) investigated hepatic injury due to exposure to chromium trioxide from chromic acid mist. Of five patients with high urinary chromium concentrations, two showed clinical evidence of hepatic involvement and another had no physical evidence of systemic disease. One of the patients with symptoms was jaundiced and one patient had hepatic tenderness. Biopsy on four of the five patients showed abnormalities in hepatic structure. The authors concluded that subtle systemic intoxication to employees in the chromium industry may be a definite health hazard.

Evan and Dail (1974) studied structural changes in the kidney following chromate treatment. Sodium chromate (10 or 20 mg/kg wt) injected intraperitoneally into rats induced changes which correlated with the amount of lysozyme in the urine. The chromate selectively affected the cells in the convoluted portion of the proximal tubule; progressive changes were swelling and loss of microvilli, formation of intracellular vacuoles, mitochondrial swelling, and cytoplasmic liquefaction followed by desquamation. Higher chromate doses and longer exposure caused greater damage. Urinary lysozyme concentrations increased as damage to the tubule cells became more severe.

The effects of adding chromium to the drinking water of animals have been studied. For four years dogs were given water containing from 0.45 to 11.2 ppm chromate (Anwar et al., 1961). Chromium accumulated in the liver, kidney, and spleen independent of the chromium concentration in water. No significant pathological changes were found in any of the animals. Administering both trivalent and hexavalent chromium (25 ppm) in drinking water to rats for a year produced no toxic symptoms. Hexavalent chromium produced higher tissue chromium concentrations than trivalent chromium; therefore, its ingestion may be potentially more hazardous. Byerrum (1960) also introduced hexavalent chromium into the drinking water of rats. In agreement with Anwar et al. (1961), he found no toxicity due to the chromium.

6.3.3.4 Mutagenesis and Teratogenesis — No data were found implicating chromium as either a mutagen or a teratogen.

6.3.3.5 Recommended Threshold Limit Values — The threshold limit values (TLV) recommended by the American Conference of Governmental Industrial Hygienists in 1970 for airborne chromium compounds in the work environment vary according to the chromium form. For chromic acid and chromates expressed as CrO_3, the TLV is 0.1 mg/m^3. For other soluble chromic and chromous salts, the TLV is 0.5 mg/m^3 expressed as chromium. For the metal and its insoluble salts, the TLV is 1 mg/m^3 (Smith, 1972). The same organization has recommended a TLV of 0.1 mg/m^3 for some insoluble chromates (National Academy of Sciences, 1974).

The National Institute for Occupational Safety and Health (NIOSH) of the U.S. Department of Health, Education, and Welfare has recommended that the TLV for chromic acid be 0.05 mg/m^3 as chromium trioxide, with a ceiling concentration of 0.1 mg/m^3, as determined by a sampling time of 15 min (U.S. Department of Health, Education, and Welfare, 1973). These levels may be low enough to prevent manifestation of most effects of chromium exposure. However, according to Smith (1972), if an air quality standard for chromium is adopted for the general population, it can be expected to be very much lower than the TLV.

Controls more stringent than those indicated by the limits cited above have recently been recommended by NIOSH for both soluble (noncarcinogenic) and insoluble (carcinogenic) airborne chromium(VI) compounds. The maximum workplace concentration of airborne carcinogenic chromium(VI) recommended is 1 μg/m^3 of breathing zone air; carcinogenic chromium(VI) is defined as poorly soluble monochromates and dichromates (U.S. Department of Health, Education, and Welfare, 1975). The maximum recommended concentration for airborne, noncarcinogenic hexavalent chromium — defined as the readily soluble monochromates and dichromates — is considerably higher: 25 μg chromium(VI) per cubic meter of breathing zone air determined as a time-weighed average exposure for up to a 10-hr workday, 40-hr workweek. For any 15-min sample, the permissible maximum concentration is 50 μg chromium(VI) per cubic meter of breathing zone air.

SECTION 6

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SECTION 7

ENVIRONMENTAL DISTRIBUTION AND TRANSFORMATION

7.1 SUMMARY

Chromium is an abundant element. Large amounts are used in the transportation industry, construction, machinery, and refractory products. Lesser amounts are also used for home appliances, pigments and paints, leather tanning, and metal plating. The entire U.S. chromium ore supply is imported from other countries, including South Africa, the U.S.S.R., Turkey, the Philippines, and Albania. The world supply of chromium is adequate to meet U.S. demands until at least the year 2000.

Chromium is emitted into the atmosphere mainly from ore refining, chemical processing, refractory processing, fossil fuel combustion, cement processing, asbestos production, and incineration of a variety of materials. Air chromium concentrations exceeded 10 ng/m^3 in 59 of 186 urban areas examined and are below the detection limit in most nonurban areas. Atmospheric chromium is usually in particulate form. Background levels are difficult to estimate but may be about 5 pg/m^3.

Total soil chromium concentrations vary, ranging from <5 to about 300 ppm except in serpentine soils which may have up to 1% to 2%. Available chromium is quite low (0.01 to 4 ppm) even in serpentine soils. Most chromium in soil is in an insoluble or tightly bound trivalent form.

Chromium concentrations in fresh water range from 0 to about 100 ppb. Seawater concentrations are lower (0 to 0.36 ppb). Both trivalent and hexavalent chromium exist in water, but the trivalent form may eventually precipitate or be absorbed from the water. Hexavalent chromium is the major stable form in seawater.

Chromium concentrations in sediments range from <1 to about 100 ppm, which corresponds to background levels. The anthropogenic input has not been high.

Precipitation and fallout remove chromium from the atmosphere to both land and water. Chromium within soil is insoluble and leaching removes very little. Surface runoff supplies some chromium to natural waters, where it is eventually deposited in sediments. Management of aqueous chromium wastes usually involves converting any hexavalent chromium to the trivalent form. The pH is raised to 9.5 and chromic hydroxide precipitates. The dried precipitate is placed in landfills.

Sewage sludge contains a wide range of chromium concentrations (20 to 40,000 ppm) and is often added to soils as fertilizer. The chromium within these amended soils is not easily extractable and, thus, is neither available for plants nor lost by leaching. Other toxic elements in sludges are of much greater concern.

7.2 TRENDS IN PRODUCTION AND USAGE

Chromium is present in a variety of rocks (Mertz et al., 1974) (Table 7.1). Ultramafic and serpentine rocks contain the largest chromium concentrations; granitic rocks, limestones, and dolomites contain the smallest amounts. Chromium in igneous rocks, usually in the mineral form of chromite, shows positive correlation with magnesium and nickel content. Argillaceous sedimentary rocks also contain chromium, which is usually concentrated in the phosphorites and in bauxite and lateritic iron ores. Frohlich (1960) in his study of the geochemistry of chromium found:

> The analyses show that chromium is concentrated in the basic and ultrabasic rocks, while the granites investigated generally contained only about 1 p.p.m. Cr. In the basic rocks, the chromium is present in specific chromium minerals such as chromite and picotite, and also in magnetites and pyroxenes. The felspar contains almost no chromium.

Table 7.1. Chromium content of various materials (ppm)

Type of material	Chromium content	
	Usual range reported	Average
Ultramafic and serpentine	1100–3400	1800
Basalts and gabbros	60–420	200
Andesites, diorites	10–200	50
Granitic rocks	2–60	5
Limestones and dolomites		11
Sandstones		35
Clays and shales	1–200	90
Soils	10–150	40
Phosphorites	30–3000	300[a]
Coal		10

[a] Phosphorites from Idaho, Wyoming, and Utah average close to 1000 ppm chromium.

Source: Adapted from Mertz et al., 1974, Table 10, p. 30. Reprinted by permission of the publisher.

The chromium content of volcanic rocks decreases steadily with increasing SiO_2 content. Thus, the melilite basalt of Gotzenbruhl with 34.7% SiO_2 contains 1380 p.p.m. Cr, while the Aar granite with 77% SiO_2 contains but 1 p.p.m. Cr.

Among the sedimentary rocks, high chromium contents are found in bauxites and in sedimentary iron ore deposits. In the bauxites this is due to relative (secondary) enrichment of chromium, while in the iron ores chromium may be associated with the iron in a colloidal state.

Pelitic sediments show a very uniform chromium content. Of 40 samples investigated, 24 contained between 70 and 100 p.p.m. Cr, while the remainder were also fairly close to these values.

For the most part, the chromium in sediments is concentrated in the micas and clay minerals, particularly in illite.

Chromite, which may be represented as $(Mg, Fe)O \cdot (Cr, Al, Fe)_2O_3$, is the major chromium mineral of commercial importance. In the United States, unaltered forms range in composition from 16.4% to 60.4% Cr_2O_3 (Thayer and Miller, 1962). United States chromite deposits occur in Maryland, Montana, North Carolina, Pennsylvania, Texas, Wyoming, California, in beach-sand deposits in Oregon and Washington, and in lateritic iron ores in Washington. These deposits are small and presently of no commercial value (Mertz et al., 1974). Major minable reserves of chromite (containing 33% to 55% Cr_2O_3) exist in Brazil, Cuba, Rhodesia, and the Republic of South Africa; several other countries have smaller minable amounts (Thayer, 1973) (Table 7.2). Additional estimates of chromite ore resources are given in Table 7.3.

Because of its importance for various defense purposes, chromium ore is stockpiled, and "due to the politically unstable nature of the supply of chromium ore, stockpiles tend to be larger than ordinarily expected" (GCA Corporation, 1973). Stockpile inventories for 1972 were 826,000 metric tons of chemical-grade chromite, 1,061,000 metric tons of refractory-grade chromite, 1,413,000 metric tons of metallurgical-grade chromite, 366,000 metric tons of high-carbon ferrochromium, 290,000 metric tons of low-carbon ferrochromium, 54,000 metric tons of ferrochromium-silicon, and 7300 metric tons of chromium metal (Morning, 1974).

The United States currently imports all of its chromium ore. In 1968, about 75% came from South Africa and the U.S.S.R. and about 25% from Turkey, the Philippines, and Albania (Brantley, 1970). Amounts of chromite imported in 1972 were 394,000 metric tons from the U.S.S.R, 92,000 metric tons from Turkey, 225,000 metric tons from the Republic of South Africa, 84,000 metric tons from Southern Rhodesia, 119,000 metric tons from the Philippines, 25,000 metric tons from Pakistan, 12,000 metric tons from the Malagasy Republic, and 13,000 metric tons from Iran (Morning, 1974).

Table 7.2. Estimated world reserves and resources of chromite ore (metric tons)

Area	Type of ore[a] and deposit[b]	Identified chromium resources[c]		Hypothetical[f] and speculative[g] resources
		Reserves[d]	Conditional resources[e]	
Western Hemisphere				
United States	A (P)	None	350	500
	B, B- (S, Pl)	None	5,000	2,000
	C (P)	None	100	100
Brazil	A (S)	2,500	3,000	5,000
	B (S)	3,500	2,000	
	C (P)	100	150	
Canada	A (P)		100	
	B, B- (S)		2,500	5,000
Cuba	A (P)		100	
	C (P)	250	1,000	1,000
Greenland	B- (S)		10,000	10,000+
Other areas			200	200
Hemisphere total	A	2,500	3,650	5,500
	B	3,500		17,000+
	B-		19,500	
	C	350	1,200	1,100
	Other		200	200
	All types	6,350	24,550	23,800+
Eastern Hemisphere				
Republic of South Africa	A (S)	500,000	500,000	3,000,000+
	B (S)	1,000,000	2,000,000	
Rhodesia	A (S, Pl)	500,000	500,000	500,000+
	B (S)	50,000	50,000	
U.S.S.R.	A (P)	10,000	10,000	25,000
	B- (S)	1,000	2,000	
	C (P)	10,000	10,000	
Turkey	A (C) (P)	5,000	5,000	5,000
Finland	B (S)	10,000	5,000	10,000
India	A (S, P)	5,000	4,000	20,000
	B (S)	2,000	2,000	
Philippine Republic	A (P)	700	500	1,000
	C (P)	4,000	2,000	5,000
Malagasy Republic	A (S)	4,000	3,000	7,000
	B (S)	1,000	2,000	
Iran	A (P)	1,500	1,000	5,000
Greece	A (P)	50	100	250
	C (P)	50		
Other areas	A (C) (P)	2,000	2,000	2,500
	B (S)			
Hemisphere total	A	577,250	574,550	3,581,250
	B	1,064,020	2,060,000	
	B-	1,000	2,000	
	C	14,050	12,050	
	All types	1,656,300	2,648,600	3,581,250
World total (rounded)		1,663,000	2,675,000	3,600,000

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[a] Types of ore: A, high chromium ore, Cr_2O_3 more than 46%, Cr:Fe is more than 2:1; B, high-iron ore, Cr_2O_3 40-46%, Cr:Fe is 1.5:1 to 2:1; B-, high iron ore, Cr_2O_3 less than 40%, Cr:Fe is 1.5:1 or less; C, high-aluminum ore, Al_2O_3 is more than 20%, Al_2O_3 + Cr_2O_3 is more than 60%.

[b] Types of deposit: (S), layered or stratiform; (P), pod-shaped; (Pl), placer, subordinate; (C), amount not estimated.

[c] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[d] Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.

[e] Conditional resources: Specific, identified mineral deposits whose contained minerals are not profitably recoverable with existing technology and economic conditions.

[f] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

[g] Speculative resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that may exist in unknown districts or in unconventional form.

Source: Adapted from Thayer, 1973, Table 24, pp. 117-118. Data collected from several sources.

Table 7.3. Estimated world chromite ore resources

Area	Total (thousand metric tons)	High chromium[a]		High iron[b]		High aluminum[c]	
		Percent	Quantity (thousand metric tons)	Percent	Quantity (thousand metric tons)	Percent	Quantity (thousand metric tons)
Republic of South Africa	2,000,000	5	100,000	95	1,900,000	10	1,000
Southern Rhodesia	600,000	50	300,000	50	300,000		
Turkey	10,000	90	9,000			10	1,000
United States	8,000	5	400	92.5	7,100	2.5	200
Philippines	7,500	20	1,500			80	6,000
Finland	7,500			100	7,500		
Canada	5,000			100	5,000		
Other	11,350	72	8,175	2	200	26	2,975
Free world total	2,649,350	16	419,075	84	2,220,100	0.4	10,175
U.S.S.R. and other Communist countries	51,500	51	26,500	29	15,000	20	10,000
World total (rounded)	2,701,000	17	446,000	83	2,235,000	1	20,000

[a] Cr_2O_3, 45% or more, metallurgical ores.
[b] Cr_2O_3, 40% or more, chemical ores.
[c] Al_2O_3, 20% or more, refractory ores.

Source: Adapted from Brantley, 1970, Table 2, p. 251.

In 1972, the U.S. chromium consumption was 320,000 metric tons, which represented 1,034,000 metric tons of chromite ore; 63.8% was used by the metallurgical industry, 19.6% by the refractory industry, and 16.6% by the chemical industry (Morning, 1974). Figure 7.1 presents the chromium supply-demand relationships for 1968. Most uses of chromium depend upon its decorative and corrosion-resistant properties. The breakdown of chromium distribution into specific categories (Figure 7.1 and Table 7.4) shows that construction products, transportation machinery and equipment, and refractory products consumed most of the 458,000 metric tons which were used in 1968 (Brantley, 1970). Metallurgical uses include iron castings, chrome alloys, steels and stainless steel, and various chrome-plated items (Brantley, 1970). Because chromite has a high melting point [2038°C (3700°F)] and is chemically inert, it is used in manufacturing bricks for lining metallurgical furnaces. A flow diagram shows the amounts of chromium used to produce various materials in 1970 (Figure 7.2).

The major chromium compounds produced in the chemical industry are chromate and dichromate, which serve as starting compounds for manufacturing all other chromium chemicals (Sullivan, 1969). This process involves roasting finely ground chromite ore with sodium carbonate and calcium carbonate and then leaching with hot water to extract "sodium monochromate" (Na_2CrO_4) (Buckell and Harvey, 1951). Addition of dilute sulfuric acid produces sodium dichromate ($Na_2Cr_2O_7$). Chromates are used for oxidation in the production of various organic materials (such as saccharin, benzoic acid, and camphor), in purification of chemicals, and in inorganic oxidations (Sullivan, 1969). A major percentage of chromic acid is used for chrome plating. Dichromate can be converted to chromium(III) sulfate, which is used in the tanning industry (6800 metric tons of Cr_2O_3 per year). Chromates and chromic oxide, in combination with other metals, produce a variety of pigments and mordants. Table 6.12 lists some important chromium compounds and their industrial uses. Fungicides and wood preservatives consume an estimated 1300 metric tons of chromium annually. Chromates are also used as rust and corrosion inhibitors.

Projected chromium demands for the year 2000 (Table 7.4) show an increase in most of the consumption categories (Brantley, 1970). The accuracy of these estimates depends on many factors. For example, the projected amount of chromium to be used in transportation depends on the total number of automobiles produced in 2000; their size, decorative requirements, and pollution control devices; the number of commercial and family vehicles; and the number of pleasure crafts, vessels, and military ships.

The supply of chromium is estimated to be adequate to meet the projected demand (for the year 2000, between 0.78 and 1.16 million metric tons); however, with the present price structure, the U.S. chromium supply will be obtained entirely from foreign sources (Brantley, 1970). If domestic resources were used (U.S. reserves: 20.4 million metric tons of chromite ore with an 11.4% average Cr_2O_3 content), costs would be about $1280 per ton of chromium, compared to about $100 per ton from foreign sources. Part of the domestic demand will be supplied by recovery of chromium from stainless steel scrap and home materials scrap (<25% total).

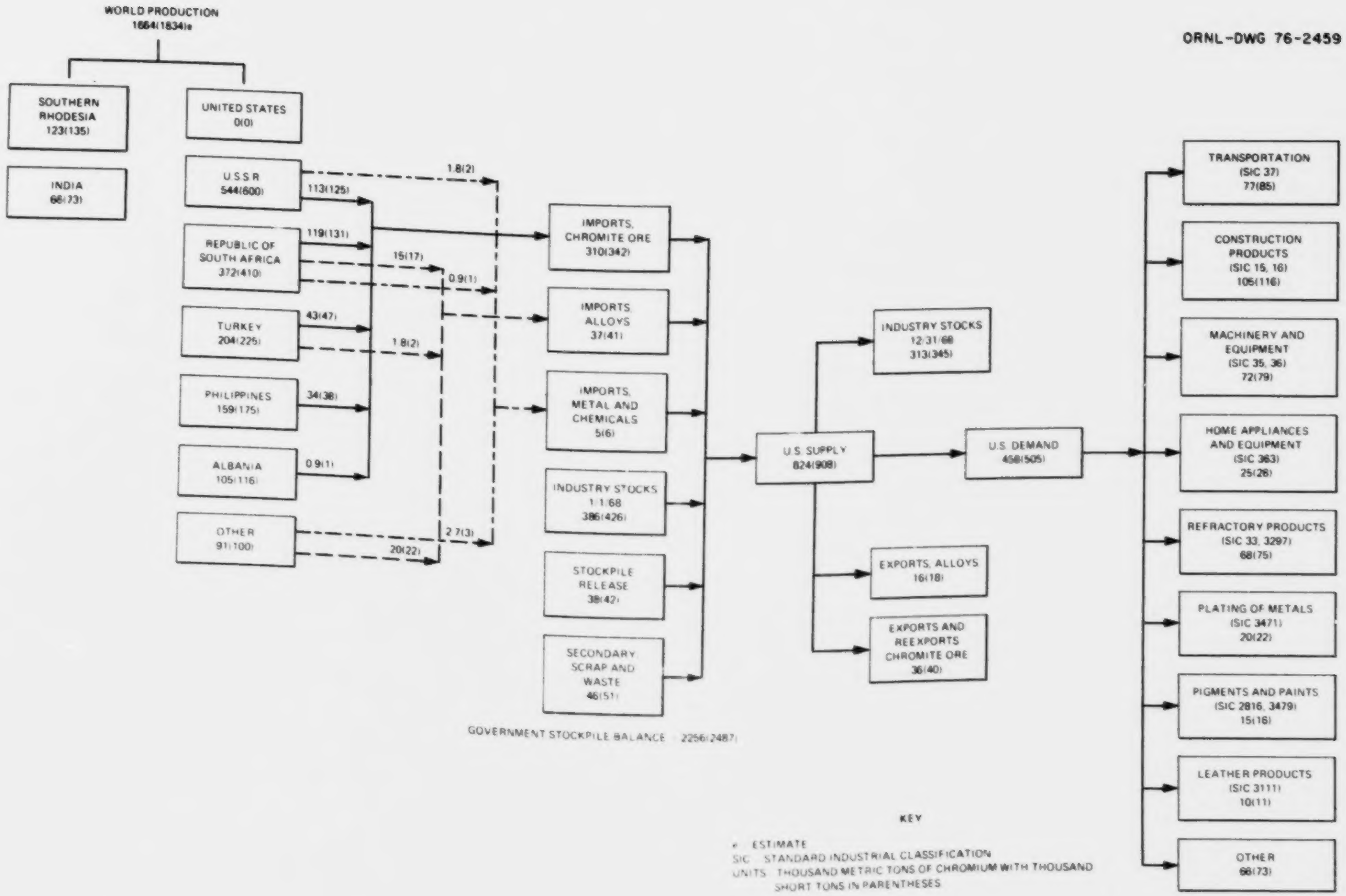

ORNL-DWG 76-2459
WORLD PRODUCTION 1664(1834)e
SOUTHERN RHODESIA 123(135)
INDIA 66(73)
UNITED STATES 0(0)
U.S.S.R 544(600)
REPUBLIC OF SOUTH AFRICA 372(410)
TURKEY 204(225)
PHILIPPINES 159(175)
ALBANIA 105(116)
OTHER 91(100)
1.8(2)
113(125)
119(131)
15(17)
0.9(1)
43(47)
1.8(2)
34(38)
0.9(1)
2.7(3)
20(22)
IMPORTS, CHROMITE ORE 310(342)
IMPORTS, ALLOYS 37(41)
IMPORTS, METAL AND CHEMICALS 5(6)
INDUSTRY STOCKS 1/1/68 386(426)
STOCKPILE RELEASE 38(42)
SECONDARY SCRAP AND WASTE 46(51)
GOVERNMENT STOCKPILE BALANCE 2256(2487)
U.S. SUPPLY 824(908)
INDUSTRY STOCKS 12/31/68 313(345)
EXPORTS, ALLOYS 16(18)
EXPORTS AND REEXPORTS CHROMITE ORE 36(40)
U.S. DEMAND 458(505)
TRANSPORTATION (SIC 37) 77(85)
CONSTRUCTION PRODUCTS (SIC 15, 16) 105(116)
MACHINERY AND EQUIPMENT (SIC 35, 36) 72(79)
HOME APPLIANCES AND EQUIPMENT (SIC 363) 25(28)
REFRACTORY PRODUCTS (SIC 33, 3297) 68(75)
PLATING OF METALS (SIC 3471) 20(22)
PIGMENTS AND PAINTS (SIC 2816, 3479) 15(16)
LEATHER PRODUCTS (SIC 3111) 10(11)
OTHER 66(73)
KEY
e ESTIMATE
SIC STANDARD INDUSTRIAL CLASSIFICATION
UNITS THOUSAND METRIC TONS OF CHROMIUM WITH THOUSAND SHORT TONS IN PARENTHESES

Figure 7.1. Supply-demand relationships for chromium, 1968. Source: Adapted from Brantley, 1970, Figure 1, p. 253.

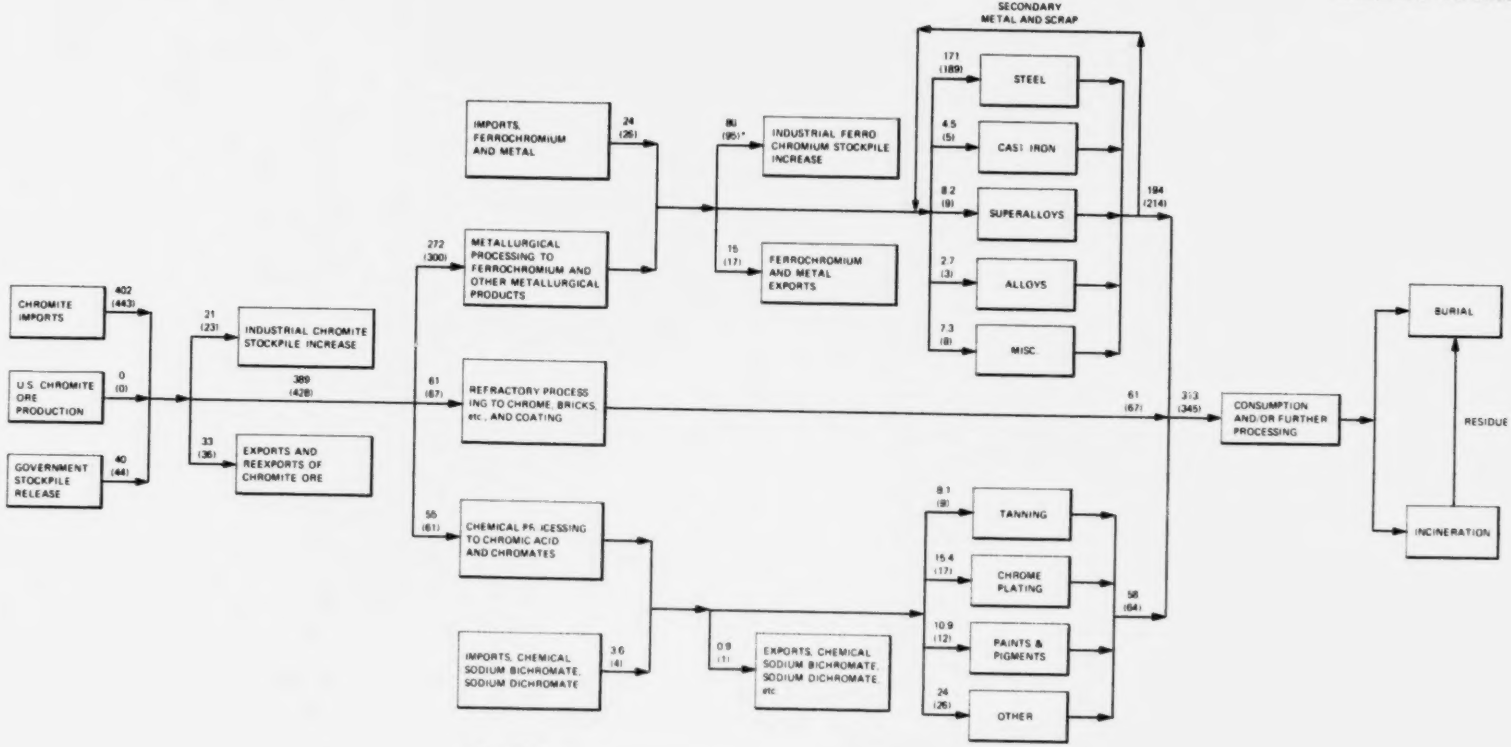
Table 7.4. Contingency forecasts of demand for chromium by end use, year 2000

End use	Demand, 1968 (thousand metric tons)	U.S. forecast base, 2000 (thousand metric tons)	Demand, 2000			
			United States		Rest of the world	
			Low estimate (thousand metric tons)	High estimate (thousand metric tons)	Low estimate (thousand metric tons)	High estimate (thousand metric tons)
Transportation	77	165	135	204	NA[a]	NA
Construction products	105	196	186	263	NA	NA
Machinery and equipment	72	191	168	259	NA	NA
Home appliances and equipment	25	89	45	91	NA	NA
Refractory products	68	50	36	68	NA	NA
Plating of metals	20	70	35	78	NA	NA
Pigments and paints	15	51	45	65	NA	NA
Leather products	10	9	9	11	NA	NA
Other	66	232	209	256	NA	NA
Total	458		868	1295	2542	3903

[a] NA = Not available.

Source: Adapted from Brantley, 1970, Table 4, p. 258.

ORNL-DWG 76-2460


SECONDARY METAL AND SCRAP
CHROMITE IMPORTS
402 (443)
U.S. CHROMITE ORE PRODUCTION
0 (0)
GOVERNMENT STOCKPILE RELEASE
40 (44)
21 (23)
INDUSTRIAL CHROMITE STOCKPILE INCREASE
389 (428)
33 (36)
EXPORTS AND REEXPORTS OF CHROMITE ORE
IMPORTS, FERROCHROMIUM AND METAL
24 (26)
272 (300)
METALLURGICAL PROCESSING TO FERROCHROMIUM AND OTHER METALLURGICAL PRODUCTS
61 (67)
REFRACTORY PROCESSING TO CHROME, BRICKS, etc., AND COATING
55 (61)
CHEMICAL PROCESSING TO CHROMIC ACID AND CHROMATES
IMPORTS, CHEMICAL SODIUM BICHROMATE, SODIUM DICHROMATE
3.6 (4)
80 (95)*
INDUSTRIAL FERRO CHROMIUM STOCKPILE INCREASE
15 (17)
FERROCHROMIUM AND METAL EXPORTS
0.9 (1)
EXPORTS, CHEMICAL SODIUM BICHROMATE, SODIUM DICHROMATE, etc.
171 (189)
STEEL
4.5 (5)
CAST IRON
8.2 (9)
SUPERALLOYS
2.7 (3)
ALLOYS
7.3 (8)
MISC.
8.1 (9)
TANNING
15.4 (17)
CHROME PLATING
10.9 (12)
PAINTS & PIGMENTS
24 (26)
OTHER
194 (214)
61 (67)
58 (64)
313 (345)
CONSUMPTION AND/OR FURTHER PROCESSING
BURIAL
RESIDUE
INCINERATION

*GCA ESTIMATES

UNITS THOUSAND METRIC TONS CONTAINING CHROMIUM WITH THOUSAND SHORT TONS IN PARENTHESES

Figure 7.2. Chromium material flow, 1970. Source: Adapted from GCA Corporation, 1973, Figure 1, p. 3.

With advances in technology, use of substitute materials, and development of new uses, changes in demand could occur. From a production viewpoint, the substitution of chemical grades of chromite for metallurgical grade is to be expected in the near future for some uses (Brantley, 1970). In the production of stainless steels, lower cost high-carbon ferrochromium is increasing in use compared to low-carbon ferrochromium. These steels have a slightly lower chromium content than the steels they replace and have a comparable strength and corrosion resistance. The trend is toward expanded use of heat- and corrosion-resistant materials and use of lower grades of chromite for their production in some cases.

7.3 DISTRIBUTION OF CHROMIUM IN THE ENVIRONMENT

7.3.1 Sources of Pollution

Major sources of atmospheric chromium emissions are from different aspects of the chromium industry, such as ore refining, chemical processing, refractory processing, metallurgical processing, and "inadvertent" sources such as coal and oil combustion, cement production, incineration, and asbestos production (GCA Corporation, 1973) (Table 7.5). Ferrochromium production is by far the major source of atmospheric emissions (68.2% of the U.S. total). Emission control procedures decreased total chromium emissions by 54% [16,463 metric tons per year (18,136 tons per year) after control compared with 36,106 metric tons per year (39,775 tons per year) before control] with a 40% reduction in the ferrochromium industry (Table 7.5).

Data for geographical distribution of atmospheric chromium emissions in the United States, divided according to the U.S. Environmental Protection Agency regions, are presented in Table 7.6. The more populated, industrial areas of the United States received the most emissions. The Great Lakes area received 29% of the total chromium emissions, while the three East Coast regions were next with 19.0%, 18.5%, and 17.3%. The rest of the United States received very little.

Another study of atmospheric chromium emissions (Goldberg, 1973) gave similar estimates for primary chromium production, but it did not consider emissions from the ferrochromium industry (Table 7.7). In addition, estimated total emissions from coal and oil combustion were considerably higher. Thus, from these two studies, total emissions were estimated to be between 11,000 and 16,000 metric tons per year.

Chromium air pollution comes mainly from the industrial production of chrome alloys and chromium metal, from chemical industries, and from the use of chromium chemicals or end products. Chromium has not been mined in the United States since 1961, so no air pollution can be attributed to this source.

Cement production also releases chromium to the atmosphere and to water. A typical analysis of portland cement showed 41.2 ppm chromium (range 27.5 to 60 ppm), of which 4.1 ppm was soluble and of this amount, 2.9 ppm was hexavalent (Schroeder, 1970). In 1970, about 250 metric tons of chromium was released to the atmosphere by cement production industries (GCA Corporation, 1973).

Table 7.5. Sources and estimates of chromium-containing atmospheric emissions in 1970

Source	Uncontrolled emission factor (kg/10³ kg)	Production level (metric tons/year)	Chromium in emissions (%)	Emissions of chromium before controls (metric tons/year)	Estimated level of emission control (%)	Emissions of chromium after controls (metric tons/year)	Percent of total U.S. chromium emissions
Mining							
None in United States				0			
Refining							
Ferrochromium							
Electric furnace	(100–415) 250[a]	341,000	22	18,700	40	11,200	68.2
Material handling	5	341,000	65	1,100	32	750	4.6
Electrolytic chromium	0.024	8,200	51	Negligible	95	Negligible	
Refractory							
Noncast	75	55,000	*b*	4,100	64	1,500	9.0
Electric cast	112	6,000	*b*	684	77	150	1.0
Chemical processing							
Dichromate	15	55,400	*b*	835	90	84	
Other chemicals						22	0.6
Steel and alloys							
Chromium steels	12	172,000	*b*	2,100	78	472	2.9
Cast iron	38	4,500	*b*	171	99	1.8	0
Super alloys and alloys	12	11,000	*b*	136	78	30	0.2
General steel making	NA[c]	NA	NA	NA	NA	91	0.6
Inadvertent sources							
Coal combustion	NA	30,700,000	0.026	7,900	82	1,420	8.6
Oil combustion	NA	261,000	0.13	336	0	336	2.0
Cement production	NA	848,000	0.03	NA	NA	254	1.5
Incineration	NA	845,000	0.017	NA	NA	143	0.9
Asbestos	NA	6,000	0.15	9.1	99	0	
Total				36,100	54	16,500	

[a] Intermediate value.

[b] Emission factor multiplier equal to tons of chromium processed or handled annually.

[c] NA = Not applicable.

Source: Adapted from GCA Corporation, 1973, Table 2, p. 12.

Table 7.6. Regional distribution of principal chromium sources and emissions

Environmental Protection Agency region	Ferrochrome production[a]		Refractory production[a]		Chrome steel production[a]		Cement production[b]		Chromium emissions from coal production[b]		Chromium emissions from oil combustion[b]		Total chromium emissions	
	Number of plants	Chromium emissions (metric tons per year)	Number of plants	Chromium emissions (metric tons per year)	Number of plants	Chromium emissions (metric tons per year)	Number of plants	Chromium emissions (metric tons per year)	(metric tons per year)	Percent of total oil derived	(metric tons per year)	Percent of total oil derived	(metric tons per year)	Percent of total U.S. chromium emissions
I. Conn., Me., Mass., N.H., R.I., Vt.	0	0	0	0	9	30	1	1.8	10	0.7	61	18.0	103	0.6
II. N.J., N.Y., P.R., V.I.	3	2,600	4	160	56	180	13	18	81	5.7	98	29.1	3,140	19.0
III. Del., Md., Pa., Va., W.Va., D.C.	2	1,700	15	610	33	110	28	39	310	21.7	50	15.0	2,800	17.3
IV. Ala., Fla., Ga., Ky., Miss., N.C., S.C., Tenn.	3	2,600	2	82	3	9	27	38	300	21.0	32	9.6	3,000	18.5
V. Ill., Ind., Mich., Minn., Ohio, Wis.	4	3,500	14	570	33	110	30	41	580	44.1	25	7.6	4,830	29.0
VI. Ark., La., N.M., Okla., Tex.	0	0	0	0	1	3.6	27	38	20	1.4	13	3.7	74	0.5
VII. Iowa, Kan., Mo., Neb.	0	0	2	82	2	6.3	20	28	58	4.1	2.7	0.9	177	1.1
VIII. Col., Mont., N.D., S.D., Utah, Wyo.	0	0	1	41	0	0	9	13	47	3.3	6.3	1.8	107	0.7
IX. Ariz., Calif., Nev., Hawaii, South Pacific	0	0	2	82	5	16.3	19	27	10	0.7	39	11.6	174	1.1
X. Alaska, Idaho, Ore., Wash.	1	860	0	0	1	3.6	7	10	4.5	0.3	9	2.7	898	5.4
Total	13	11,300	40	1,630	143	470	181	254	1,420	100	336	100	15,300	93.2

[a] Chromium industry source.
[b] Inadvertent source.

Source: Adapted from GCA Corporation, 1973, Table 4, p. 22.

Table 7.7. Chromium emission sources

Source	Chromium emission (metric tons)	Chromium emission Percent of this pollutant
Asbestos mining	7.3	0.07
Kraft pulp mill recovery furnace	Negligible	Negligible
Sulfite pulp mill	Negligible	Negligible
Primary chromium production	3,800	34.98
Asbestos products	Negligible	Negligible
Refractory brick production	6.3	0.06
Installation of asbestos material	Negligible	Negligible
Spray-on fireproofing	Negligible	Negligible
Use of insulating cement	Negligible	Negligible
Power plant boilers		
Pulverized coal	5,100	46.40
Stoker coal	580	5.33
Cyclone coal	170	1.60
All oil	20	0.18
Industrial boilers		
Pulverized coal	220	2.06
Stoker coal	780	7.20
Cyclone coal	110	1.02
All oil	15	0.14
Residential/commercial boilers		
Coal	70	0.64
Oil	34	0.32
Total	10,900	

Source: Adapted from Goldberg, 1973, Appendix A, p. 107.

The combustion of natural materials is another source of atmospheric chromium. For example, coal has a relatively high chromium content which can be released during industrial and residential burning of coal (1400 metric tons of chromium for 1970). Wood and leaf burning and forest fires are also likely to release chromium, although estimated amounts were not found.

Coal combustion releases many environmental pollutants, the most abundant of which are NO_x and SO_2 (Rancitelli, Abel, and Weimer, 1974). Considerable quantities of trace elements are also released; the extent and the effects of such emissions need to be determined. Chromium emissions from the power plant in Centralia, Washington, were estimated to be 720 kg/year, with an estimated yearly deposition on soil between 3.7 and 12.9 mg/m². Eighty-two coal samples from the Illinois Basin contained 4.00 to 54.00 ppm chromium with a mean of 14.10 ppm (Ruch, Gluskoter, and Shimp, 1974). Concentrations in Belgian coal samples and in the Illinois samples were similar (Table 7.8) (Block

Table 7.8. Chromium concentrations in Belgian coal and coal ash (ppm)

Sample	Use	Chromium content
Coal	Home heating	12.0
	Electric power	55.0
	Coke production	14.2
	Industrial processes	24.5
Coal ash	Home heating	320
	Electric power	180
	Coke production	330

Source: Adapted from Block and Dams, 1975, Table II, p. 148. Reprinted by permission of the publisher.

and Dams, 1975). Chromium in Belgian coal ash ranged from 180 ppm in coal used for electric power generation to 330 ppm in coal used for coke production. Coal used in the Allen Steam Plant in Memphis, Tennessee, contained 21 ppm chromium, while slag contained 180 ppm and precipitated fly ash contained 356 ppm (White et al., 1974). Shiebly (cited in Lee and von Lehmden, 1973) reported that chromium concentrations in coal ranged between 1 and 100 ppm.

Chromium apparently has not been concentrated in coal during formation processes (Ruch, Gluskoter, and Shimp, 1974). In eight coal samples from the western United States, the ratio of the mean values of chromium in coal (9 ppm) to the clarke value for average crustal abundance of chromium (100 ppm) indicated an exclusion process. However, the significance of such estimates based on average crustal abundance figures is in doubt.

Although trace element concentrations in coal are small, the use of large amounts of coal releases considerable quantities of these elements to the environment. Metals have been effectively removed by grinding coal with water and then using oil to agglomerate the carbonaceous material (Capes et al., 1974). The average chromium content of feed coal was 652 ppm and that of the agglomerates was 186 ppm.

Nord and Bingham (1972) reported that Utah coals contained 22 ppm chromium and Pennsylvania coals contained 0.4 ppm chromium. They demonstrated that blood serum, lung wash fluid, and normal saline extracted various percentages of metals (magnesium, calcium, iron, and nickel) from coal samples; however, no chromium, cadmium, or lead was detected in extracts.

The use of commercial fertilizers supplies trace amounts of heavy metals to soils. Mortvedt and Giordano (1975) reported that fertilizers prepared from phosphate rock of the western United States contained higher concentrations of most heavy metals (344 ppm chromium) than those prepared from phosphate rock of the eastern United States (175 ppm chromium).

The plating and finishing industry is the major source of chromium pollution in natural waters. In New York City, electroplaters accounted for 43% of chromium received in sewage plant influent (Klein et al., 1974). Surprisingly, residential runoff accounted for 21% of chromium in the influent. This runoff perhaps came from settling of atmospheric chromium and subsequent washing into sewage waters. Chromium is released from plating processes as the result of rinsing operations; spillage; mists from hot tanks; and chromate pickling, washing, and post-plating baths (Ottinger et al., 1973). Although chromium pollution from the plating bath itself is small, the overall loss of chromium as chromates or chromic acid is very high — about 20,000 metric tons in 1970 in the United States; between 80% and 90% of the chromium becomes wastes. Recovery procedures recycle only about 30% of the wastes. Composition of some chromium-containing wastes from metal-plating industries is given in Table 7.9. Typical waste treatment involves reducing chromium(VI) to chromium(III) and subsequent raising of the pH to precipitate the hydroxide (Section 7.5).

A new process for chromium plating using chromium(III) instead of chromium(VI) is currently being tested (O'Sullivan, 1975). Advantages of this process include elimination of the spray hazard, easier disposal of spent electrolytes, more uniform chromium deposition, production of microcracked finishes, and more economical operation.

The textile industry also releases significant amounts of chromate waste, most of which is subsequently treated in the same manner as chromate wastes from other sources.

Significant progress has been made in reducing the chromium content of tannery discharge water (Eye, 1974). Examples cited for chromium removal were 97% in one instance and a decrease of chromium from 2900 ppm in the spent liquor to 0.4 ppm in the discharge solution. Chromium is usually removed by precipitation with lime.

In 1970, use of chromate compounds as pigments accounted for about 40% of the dichromates consumed in the United States (Chemical Profiles, Sodium Bichromate and Chromic Acid, as cited in Ottinger et al., 1973). Ottinger et al. (1973) estimated that 62,000 kg of chromium are lost annually in the sludge of solvent-based paints and 437,000 kg as discarded paint residues.

7.3.2 Distribution in Air

The chromium concentration in air varies with location. Sullivan (1969) cited data from the National Air Sampling Network for 1964 which gave the national average for chromium as 0.015 $\mu g/m^3$ with a maximum of 0.350 $\mu g/m^3$. Table 7.10 gives chromium content of air in 1968-1969 for both urban and nonurban areas (U.S. Environmental Protection Agency, 1973). Although chromium

Table 7.9. Composition of chromium-containing wastes from metal plating industries

Waste description	Form	Source
3000 ppm of a mixture of chromium, 20% aluminum sulfate, and 35% sulfuric acid (trace of copper, nickel, lead)	Liquid	Aluminum anodizing bath with drag out
12.5% chromic acid-dichromate in 10% to 30% sulfuric acid with 5000 to 120,000 ppm chromium [85% as Cr(III)] with 100 to 1000 ppm lead, copper, and iron	Liquid	Metal finishing
Dilute chromic acid solution containing Cr(III) at 100 to 200 ppm and Cr(VI) at 2000 to 4000 ppm with traces of organics (combined wash waters)	Liquid	Metal plating
Partially neutralized aqueous plating waste containing 5 to 10% zinc chromate, and 5 to 10% zinc phosphate contaminated with various organic oils	Liquid	Zinc plating
Solutions of chromates and dichromates in sulfuric acid (6 to 12%) containing 5000 to 170,000 ppm chromium with copper, lead, and traces of organics	Liquid	Formation of protective and decorative coatings (metals)
0.1 to 0.5% chromium, 100 to 400 ppm copper, 100 to 600 ppm nickel in 5 to 10% aqueous hydrofluoric-hydrochloric acid	Liquid	Plating preparation (metal)
1 to 20% chromium in solids concentrations of 10 to 80% from settling and/or dewatering processes; includes copper in varying amounts with varying amounts of inert filter aids	Sludge	Chemical process (plating operations, manufacturing, metallurgical)
100 to 1000 ppm chromium as alkaline cyanide solutions (6 to 20%) with copper in varying amounts with possible traces of organics, nickel, lead, and zinc	Liquid	Metal plating (formation of protective and decorative coatings)
5 to 6% chromic acid in water solution with 1% iron	Liquid	Metal plating, shipbuilding
9% chromic acid in 13% aqueous sulfuric acid	Liquid	Metal finishing and plating
0.1 to 1% sodium or potassium dichromate in water, usually sulfuric acid present in a 1 to 15% concentration	Liquid	Metal finishing, shipbuilding, plating

Source: Adapted from Ottinger et al., 1973, Table 1, p. 147.

concentrations in most nonurban areas, and even in many urban areas, were below detection levels, certain areas did have measurable levels at some time during the year. Yearly average concentrations in urban areas varied from below detection level to as high as 0.120 μg/m^3 in Baltimore, Maryland. Yearly averages were greater than 0.010 μg/m^3 in only 59 of 186 urban areas. In fact, chromium in the air has apparently declined in many, but not all, U.S. cities since 1959 (Table 7.11) (Schroeder, 1970). Table 7.12 reports chromium values in air compiled from several sources; these values are similar to those found by the National Air Surveillance Network.

Lee, Patterson, and Wagman (cited in Bond, Straub, and Prober, 1972) found that the air in Cincinnati, Ohio, and in suburban Fairfax, Ohio, had similar chromium content (0.31 and 0.28 μg/m^3, respectively), while a wildlife preserve had a somewhat lesser concentration. On another day, air

Table 7.10. Chromium concentrations in urban and nonurban air, quarterly composites and yearly averages, 1969
($\mu g/m^3$)

Location	First quarter	Second quarter	Third quarter	Fourth quarter	Yearly av
		Urban areas			
Alabama					
Gadsden	0.0	0.0	0.0	0.0	
Huntsville	0.0	0.0	0.0	0.0	
Mobile	0.0	0.0	0.013	0.0	
Montgomery	0.0	0.0	0.0	0.0	
Alaska					
Anchorage	0.0	0.0	0.0	0.0	
Fairbanks	0.0	0.0	0.0	0.0	
Arizona					
Maricopa County	0.0	0.0	0.0	0.0	
Phoenix	0.0	0.0	0.0	0.0	
Tucson	0.0	0.0	0.0	0.0	
Arkansas					
Little Rock	0.0	0.0	0.0	0.0	
Texarkana	0.0	0.0	0.0	0.0	
West Memphis	0.013	0.0	0.017	0.0	
California					
Anaheim	0.0	0.0	0.0	0.0	
Burbank	0.010	0.010	0.014	0.015	0.012
Fresno	0.0	0.0	0.0	0.0	
Glendale	0.0	0.0	0.0	0.0	
Long Beach	0.0	0.012	0.014	0.0	
Los Angeles	0.015	0.018	0.019	0.019	0.018
Oakland	0.011	0.014	0.017	0.014	0.014
Ontario	0.0	0.014	0.012	0.012	0.010
Riverside	0.0	0.012	0.009	0.010	0.009
Sacramento	0.0	0.0	0.0	0.0	
San Bernardino	0.011	0.020	0.016	0.023	0.017
San Diego	0.022	0.017	0.010	0.013	0.015
San Francisco	0.0	0.0	0.0	0.0	
San Jose	0.0	0.0	0.0	0.0	
Santa Ana	0.0	0.0	0.0	0.0	
Torrance	0.0	0.010	0.016	0.0	
Colorado					
Denver	0.010	0.017	0.014	0.0	0.011
Montezuma County	0.0	0.0	0.0	0.0	
Connecticut					
Bridgeport	0.0	0.027	0.013	0.008	0.013
Hartford	0.0	0.0	0.014	0.011	
New Haven	0.009	0.0	0.0	0.0	
Waterbury	0.014	0.017	0.013	0.019	0.016

Table 7.10 (continued)

Location	First quarter	Second quarter	Third quarter	Fourth quarter	Yearly av
Delaware					
Wilmington	0.017	0.013	0.020	0.0	0.013
Dist Columbia					
Washington	0.0	0.016	0.0	0.0	
Florida					
Jacksonville	0.020	0.0	0.013	0.013	0.012
Miami	0.0	0.0	0.0	0.0	
St. Petersburg	0.010	0.0	0.015	0.009	0.009
Tampa	0.015	0.014	0.020	0.012	0.015
Georgia					
Atlanta	0.0	0.0	0.015	0.0	
Columbus	0.0	0.0	0.0	0.0	
Savannah	0.0	0.0	0.0	0.011	
Hawaii					
Honolulu	0.0	0.0	0.008	0.0	
Idaho					
Boise City	0.0	0.0	0.0	0.0	
Illinois					
Chicago	0.014	0.012	0.016	0.024	0.016
East St. Louis	0.012	0.0	0.0	0.120	
Joliet	0.012	0.015	0.017	0.0	0.012
North Chicago	0.0	0.0	0.013	0.015	
Peoria	0.0	0.016	0.014	0.010	0.011
Rockford	0.0	0.010	0.019	0.014	0.011
Springfield	0.0	0.016	0.009	0.0	
Indiana					
East Chicago	0.041	0.053	0.100	0.061	0.064
Evansville	0.089	0.011	0.0	0.009	0.028
Fort Wayne	0.013	0.010	0.022	0.0	0.012
Gary	0.018	0.016	0.013	0.016	0.016
Hammond	0.024	0.021	0.015	0.018	0.019
Indianapolis	0.015	0.013	0.012	0.013	0.013
New Albany	0.018	0.013	0.010	0.012	0.013
South Bend	0.0	0.010	0.0	0.010	
Terre Haute	0.0	0.0	0.0	0.0	
Iowa					
Davenport	0.013	0.011	0.032	0.017	0.018
Des Moines	0.0	0.0	0.0	0.0	
Dubuque	0.0	0.0	0.0	0.0	
Kansas					
Kansas City	0.011	0.0	0.012	0.016	0.010
Topeka	0.0	0.0	0.0	0.0	
Wichita	0.0	0.0	0.0	0.0	

Table 7.10 (continued)

Location	First quarter	Second quarter	Third quarter	Fourth quarter	Yearly av
Kentucky					
Ashland	0.019	0.018	0.025	0.017	0.020
Covington	0.021	0.018	0.010	0.018	0.017
Louisville	0.019	0.010	0.012	0.016	0.014
Louisiana					
Baton Rouge	0.0	0.0	0.0	0.0	
New Orleans	0.011	0.017	0.021	0.0	0.013
Shreveport	0.0	0.008	0.0	0.0	
Maryland					
Baltimore	0.140	0.110	0.092	0.066	0.102
Massachusetts					
Boston	0.0	0.0	0.0	0.008	
Fall River	0.0	0.010	0.0	0.009	
Springfield	0.0	0.0	0.0	0.0	
Worchester	0.0	0.009	0.0	0.0	
Michigan					
Dearborn	0.014	0.014	0.017	0.047	0.015
Detroit	0.019	0.016	0.020	0.019	0.018
Flint	0.012	0.010	0.011	0.0	0.009
Grand Rapids	0.015	0.008	0.011	0.0	0.009
Lansing	0.013	0.0	0.0	0.0	
Saginaw	0.0	0.0	0.0	0.0	
Trenton	0.015	0.010	0.0	0.010	0.009
Minnesota					
Duluth	0.0	0.0	0.0	0.014	
Minneapolis	0.012	0.0	0.0	0.012	
St. Paul	0.012	0.012	0.0	0.0	
Missouri					
Kansas City	0.0	0.0	0.010	0.0	
St. Louis	0.018	0.012	0.023	0.018	0.018
Montana					
Helena	0.0	0.0	0.0	0.0	
Nebraska					
Omaha	0.0	0.0	0.0	0.011	
Nevada					
Las Vegas	0.0	0.0	0.011	0.0	
Reno	0.0	0.0	0.0	0.0	
New Hampshire					
Concord	0.0	0.0	0.0	0.0	

Table 7.10 (continued)

Location	First quarter	Second quarter	Third quarter	Fourth quarter	Yearly av
New Jersey					
Burlington County	0.008	0.0	0.0	0.008	
Elizabeth	0.009	0.009	0.0	0.011	0.008
Glassboro	0.011	0.0	0.0	0.0	
Hamilton	0.0	0.010	0.018	0.009	0.010
Jersey City	0.030	0.025	0.082	0.071	0.052
Newark	0.015	0.031	0.022	0.029	0.024
Paterson	0.017	0.011	0.0	0.019	0.012
Perth Amboy	0.011	0.011	0.009	0.010	0.010
Trenton	0.011	0.0	0.0	0.016	
New Mexico					
Albuquerque	0.0	0.0	0.0	0.0	
New York					
Albany	0.009	0.010	0.0	0.011	0.008
Buffalo	0.010	0.031	0.016	0.013	0.017
New York City	0.027	0.025	0.014	0.011	0.019
Niagara Falls	0.052	0.027	0.0	0.046	0.032
Rochester	0.012	0.017	0.0	0.0	
Syracuse	0.043	0.016	0.014	0.0	0.019
Utica	0.0	0.0	0.0	0.0	
North Carolina					
Charlotte	0.011	0.0	0.0	0.0	
Durham	0.009	0.0	0.0	0.0	
Greensboro	0.012	0.0	0.0	0.0	
Winston-Salem	0.0	0.0	0.0	0.010	
North Dakota					
Bismarck	0.0	0.0	0.0	0.0	
Ohio					
Akron	0.015	0.017	0.019	0.015	0.016
Canton	0.025	0.020	0.048	0.049	0.035
Cincinnati	0.022	0.026	0.048	0.047	0.036
Cleveland	0.011	0.015	0.026	0.030	0.020
Columbus	0.014	0.015	0.012	0.009	0.013
Dayton	0.013	0.0	0.0	0.015	
Toledo	0.0	0.012	0.0	0.010	
Youngstown	0.026	0.024	0.020	0.054	0.031
Oklahoma					
Oklahoma City	0.0	0.0	0.0	0.0	
Tulsa	0.012	0.0	0.0	0.0	
Oregon					
Medford	0.0	0.0	0.0	0.0	
Portland	0.010	0.0	0.014	0.0	

Table 7.10 (continued)

Location	First quarter	Second quarter	Third quarter	Fourth quarter	Yearly av
Pennsylvania					
Allentown	0.0	0.009	0.016	0.0	
Bethlehem	0.012	0.010	0.020	0.023	0.016
Erie	0.0	0.0	0.029	0.0	
Harrisburg	0.012	0.012	0.034	0.018	0.019
Hazleton	0.0	0.0	0.0	0.0	
Johnstown	0.014	0.0	0.012	0.027	0.014
Philadelphia	0.017	0.019	0.036	0.017	0.022
Pittsburgh	0.020	0.070	0.069	0.042	0.050
Reading	0.049	0.085	0.070	0.052	0.064
Scranton	0.0	0.0	0.011	0.0	
Warminster	0.010	0.009	0.0	0.008	0.007
West Chester	0.0	0.010	0.0	0.0	
Wilkes-Barre	0.0	0.0	0.0	0.009	
York	0.022	0.0	0.012	0.009	0.011
Puerto Rico					
Bayahon	0.009	0.0	0.0	0.017	
Catano	0.0	0.021	0.013	0.015	0.013
Guayanilla	0.0	0.014	0.009	0.0	
Ponce	0.0	0.0	0.0	0.0	
San Juan	0.0	0.0	0.013	0.0	
Rhode Island					
East Providence	0.0	0.0	0.0	0.0	
Providence	0.0	0.0	0.0	0.0	
South Carolina					
Columbia	0.0	0.0	0.0	0.0	
Greenville	0.0	0.0	0.0	0.031	
Tennessee					
Chattanooga	0.023	0.022	0.011	0.013	0.017
Knoxville	0.009	0.009	0.014	0.0	0.009
Memphis	0.022	0.0	0.0	0.016	
Nashville	0.013	0.015	0.012	0.016	0.014
Texas					
Dallas	0.013	0.014	0.0	0.015	0.011
El Paso	0.0	0.0	0.0	0.0	
Fort Worth	0.0	0.0	0.0	0.011	
Houston	0.011	0.011	0.0	0.0	
Pasadena	0.010	0.0	0.036	0.0	
San Antonio	0.0	0.0	0.0	0.0	
Utah					
Ogden	0.0	0.0	0.0	0.0	
Salt Lake City	0.0	0.015	0.023	0.013	0.013

Table 7.10 (continued)

Location	First quarter	Second quarter	Third quarter	Fourth quarter	Yearly av
Vermont					
Burlington	0.0	0.010	0.0	0.0	
Virginia					
Danville	0.0	0.012	0.0	0.011	
Hampton	0.0	0.0	0.0	0.0	
Lynchburg	0.0	0.0	0.0	0.0	
Newport News	0.009	0.0	0.0	0.0	
Norfolk	0.0	0.0	0.0	0.0	
Portsmouth	0.0	0.015	0.008	0.012	0.010
Richmond	0.0	0.0	0.0	0.0	
Roanoke	0.013	0.0	0.011	0.012	0.010
Washington					
Seattle	0.0	0.0	0.013	0.0	
Spokane	0.0	0.0	0.0	0.0	
Tacoma	0.010	0.0	0.0	0.0	
West Virginia					
Charleston	0.048	0.040	0.019	0.034	0.035
Wisconsin					
Eau Claire	0.0	0.0	0.0	0.0	
Kenosha	0.009	0.015	0.0	0.019	0.011
Madison	0.0	0.0	0.0	0.0	
Milwaukee	0.010	0.010	0.017	0.026	0.016
Racine	0.0	0.0	0.0	0.0	
Superior	0.0	0.0	0.0	0.0	
Wyoming					
Casper	0.0	0.0	0.0	0.0	
Cheyenne	0.0	0.0	0.0	0.0	
		Nonurban areas			
Arizona					
Grand Canyon National Park	0.0	0.0	0.0	0.0	
Arkansas					
Montgomery County	0.0	0.0	0.0	0.0	
California					
Humboldt County	0.0	0.0	0.0	0.0	
Florida					
Hardee County	0.0	0.0	0.0	0.0	
Idaho					
Butte County	0.0	0.0	0.0	0.0	

Table 7.10 (continued)

Location	First quarter	Second quarter	Third quarter	Fourth quarter	Yearly av
Indiana					
Monroe County	0.0	0.0	0.0	0.0	
Parke County	0.0	0.0	0.0	0.0	
Maine					
Acadia National Park	0.0	0.015	0.011	0.014	0.010
Maryland					
Calvert County	0.0	0.019	0.0	0.0	
Missouri					
Shannon County	0.0	0.0	0.0	0.0	
Montana					
Glacier National Park	0.0	0.0	0.0	0.0	
Nebraska					
Thomas County	0.0	0.0	0.0	0.0	
Nevada					
White Pine County	0.0	0.0	0.0	0.0	
New Hampshire					
Coos County	0.0	0.0	0.0	0.0	
New York					
Jefferson County	0.0	0.0	0.0	0.0	
North Carolina					
Cape Hatteras National Park	0.011	0.0	0.087	0.029	0.032
Oklahoma					
Cherokee County	0.0	0.0	0.0	0.0	
Oregon					
Curry County	0.0	0.0	0.009	0.018	
Pennsylvania					
Clarion County	0.011	0.0	0.0	0.016	
Rhode Island					
Washington County	0.0	0.0	0.0	0.0	
South Carolina					
Richland County	0.0	0.0	0.0	0.0	
South Dakota					
Black Hills National Park	0.0	0.0	0.0	0.0	

Table 7.10 (continued)

Location	First quarter	Second quarter	Third quarter	Fourth quarter	Yearly av
Tennessee					
Cumberland County	0.0	0.0	0.0		
Texas					
Matagorda County	0.0	0.0	0.0	0.0	
Vermont					
Orange County	0.0	0.0	0.0	0.0	
Virginia					
Shenandoah National Park	0.0	0.0	0.0	0.0	
Wythe County	0.0	0.0	0.0	0.0	
Wisconsin					
Door County	0.0	0.0	0.0	0.0	
Wyoming					
Yellowstone National Park	0.0	0.0	0.0	0.0	

Source: Adapted from U.S. Environmental Protection Agency, 1973, Table 5-3, pp. 5-9 – 5-12.

chromium content in Cincinnati was 0.16 μg/m³. The mass median diameter of particles, however, was very similar among the three locales (1.5 to 2.0 μm). No reason was given for the relatively high chromium contents observed in these three regions as compared to those found by the National Air Surveillance Network. Daily variation in concentrations could be expected in such studies depending upon atmospheric conditions; however, no data relating air chromium content to atmospheric stability or meteorological conditions were found. Sugimae (1975) found concentrations ranging from 0.017 to 0.087 μg/m³ in Osaka, Japan.

Little information exists on particle size distribution of the chromium in air. Cawse (1974) gave data for chromium in air particulate matter at Trebannos, United Kingdom. The mass median diameter was 1.5 μm; 12%, 12%, 12%, 17%, 10%, 7%, 9%, and 4% of total chromium was found on cascade impactor stages having effective cutoff diameters of 0.47, 0.68, 1.1, 2.3, 3.1, 5.0, 7.5, and 11.0 μm, respectively. The backing filter contained 16% of the chromium. Similar data were obtained from air in Chilton, United Kingdom; the concentration of chromium in these particles ranged from 54 to 210 ppm. There was no trend toward higher concentrations in the smaller particles.

The chromium content in fly ash from a coal-fired steam plant was 130 ppm for 25-μm particles, 130 ppm for 12.5-μm particles, 130 ppm for 10-μm particles, 300 ppm for 3.5-μm particles, and 300 ppm for 1.5-μm particles

Table 7.11. Levels of airborne chromium in U.S. cities, 1954-65 ($\mu g/m^3$)

City	Year	Chromium level	Year	Chromium level
Cities with decreasing chromium levels				
Birmingham, Ala.	1959	0.038	1965	0.005
Phoenix, Ariz.	1960	0.084	1964	0.007
Los Angeles, Calif.	1959	0.037	1963	0.015
Denver, Colo.	1959	0.019	1964	0.005
Atlanta, Ga.	1959	0.023	1965	0.002
Boise, Idaho	1960	0.020	1965	0.001
Indianapolis, Ind.	1959	0.024	1964	0.008
Des Moines, Iowa	1959	0.019	1964	0.003
Wichita, Kan.	1959	0.017	1964	0.001
New Orleans, La.	1959	0.025	1963	0.011
Baltimore, Md.	1959	0.094	1965	0.018
Boston, Mass.	1959	0.051	1964	0.007
Detroit, Mich.	1959	0.029	1964	0.014
Minneapolis, Minn.	1959	0.020	1964	0.002
St. Louis, Mo.	1959	0.041	1964	0.007
Las Vegas, Nev.	1961	0.031	1964	0.001
Camden, N.J.	1962	0.014	1963	0.010
Newark, N.J.	1961	0.046	1964	0.020
Albuquerque, N.M.	1960	0.057	1965	0.002
New York, N.Y.	1959	0.021	1964	0.006
Charlotte, N.C.	1959	0.023	1964	0.002
Akron, Ohio	1960	0.041	1965	0.009
Cleveland, Ohio	1959	0.043	1964	0.014
Youngstown, Ohio	1959	0.047	1963	0.012
Portland, Ore.	1959	0.025	1964	0.004
Allentown, Pa.	1961	0.036	1965	0.000
Bethlehem, Pa.	1961	0.048	1965	0.005
Philadelphia, Pa.	1959	0.026	1964	0.011
Pittsburgh, Pa.	1959	0.028	1964	0.021
Chattanooga, Tenn.	1961	0.041	1964	0.015
Nashville, Tenn.	1959	0.029	1964	0.011
Houston, Tex.	1959	0.025	1964	0.004
El Paso, Tex.	1962	0.006	1964	0.000
Salt Lake City, Utah	1959	0.019	1964	0.001
Seattle, Wash.	1959	0.047	1963	0.015
Tacoma, Wash.	1959	0.018	1964	0.001
Charleston, W.Va.	1959	0.097	1964	0.044
Milwaukee, Wis.	1959	0.029	1964	0.010
Cheyenne, Wyo.	1959	0.011	1964	0.000
Mean		0.0372		0.0083

Table 7.11 (continued)

City	Year	Chromium level	Year	Chromium level
Cities with increased or unchanged chromium levels				
Pasadena, Calif.	1959	0.002	1962	0.023
San Francisco, Calif.	1959	0.001	1962	0.020
San Jose, Calif.	1959	0.001	1963	0.002
Washington, D.C.	1959	0.004	1964	0.016
East St. Louis, Ill.	1959	0.007	1963	0.029
East Chicago, Ind.	1959	0.013	1964	0.033
Rochester, N.Y.	1960	0.055	1962	0.036
Altoona, Pa.	1959	0.001	1965	0.002
Mean		0.0105		0.0201
Cities with high chromium levels				
St. Paul, Minn.	1962	0.013		
Jackson Co., Miss.	1965	0.012		
Bayonne, N.J.	1963	0.015		
Paterson, N.J.	1963	0.010		
Buffalo, N.Y.	1962	0.010		
Glen Cove, N.Y.	1962	0.019		
Troy, N.Y.	1962	0.015		
Massena, N.Y.	1961	0.019		
Mt. Vernon, N.Y.	1961	0.035		
New Rochelle, N.Y.	1961	0.022		
Asheville, N.C.	1960	0.020		
Tulsa, Okla.	1961	0.016		
Johnstown, Pa.	1963	0.010		
Lancaster, Pa.	1962	0.016		
Scranton, Pa.	1961	0.030		
Spokane, Wash.	1961	0.041		
Huntington, W.Va.	1960	0.021		
Mean		0.0191		

Source: Adapted from Schroeder, 1970, Table 2, p. 4. Reprinted by permission of the publisher.

(Lyons, cited in Lee and von Lehmden, 1973). Linton et al. (1976) demonstrated by secondary ion mass spectrometry and electron-induced x-ray spectrometry that the surface of coal fly ash had a higher concentration of chromium than material at a depth of 500 Å within the particle.

Enrichment factor analysis (chromium/cerium concentrations in fly ash or aerosol to those in soil) showed little chromium enrichment in aerosols collected at the Walker Branch Watershed, Oak Ridge, Tennessee (enrichment factor 2.0) or at the Allen Steam Plant, Memphis, Tennessee (enrichment factor 4.5) (Andren, Lindberg, and Bate, 1975). Indirect evidence for increased air chromium concentrations in the vicinity of a power plant also comes from soil analyses in which soils near the power plant contained 6.5 ppm chromium and background soils contained 4.6 ppm (Klein and Russell, 1973).

Table 7.12. Chromium concentrations in air

Area	Chromium concentration range	Reference
Bronx, N.Y.	17-73 ng/m^3	Kneip et al., 1970
Lower Manhattan, N.Y.	27-93 ng/m^3	Kneip et al., 1970
Tuxedo, N.Y.	3-23 ng/m^3	Kneip et al., 1970
San Francisco, Calif.	2-22 ng/m^3	John et al., 1973
Boston, Mass.	6.8 ng/m^3	Gordon, Zoller, and Gladney, 1973
United Kingdom	1-14 ng/kg air	Peirson et al., 1973
Lerwick, England (background)	0.9 ng/kg air	Cawse, 1974
Northwest Canada (background)	0.5 ng/kg air	Cawse, 1974
Norway (background)	0.5 ng/kg air	Cawse, 1974
Urban England	4.6-25 ng/kg air	Cawse, 1974
Heidelberg, Germany	4.6 ng/m^3	Bogen, 1974

Specific industrial activities increase the chromium content of air in their vicinities. Lee and von Lehmden (1973) reported the chromium content in particulate emissions from several sources. Chromium concentrations in emissions ranged between 1 and 100 ppm for coal-fired power plants, between 100 and 1000 ppm for cement plants, between 10 and 100 ppm for iron and steel industries, and between 100 and 1000 ppm for municipal incinerators.

Another locale with high chromium air concentrations is the area near cooling towers. Cooling-tower drift consists of water droplets formed mechanically within the tower and carried by wind into surrounding areas. Chromium (usually CrO_4^{2-}) is often used in the cooling-tower water as a corrosion inhibitor. The droplets in the cooling-tower drift are assumed to contain chromium in concentrations similar to those in the tower water. Air concentrations of chromium near a cooling tower at the Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee, were about 50 ng/m^3 for distances up to 200 m (Alkezweeny et al., 1975). Hourly chromium deposition was about 1 mg/m^2 at 30 m from the tower and about 0.01 mg/m^2 at 1000 m.

Background contamination levels are difficult to estimate because of uncertain amounts of anthropogenic input. Atmospheric chromium concentration at the South Pole, a region distant from major anthropogenic sources, was 5.3 ± 3.0 pg/m^3 with a range of 2.5 to 10 pg/m^3 (Zoller, Gladney, and Duce, 1974). The ratios of chromium to aluminum, which were the same as in the earth's crust, suggested that the chromium in the atmosphere at the South Pole was due to weathering of crustal material. By statistical correlation analysis, it was determined that chromium in air over the San Francisco Bay area was derived from soil material (John et al., 1973).

The chemical form of chromium in air depends on the source. Chromium from metallurgical production is usually in the trivalent or zero state; however, during chromate production, chromate dusts can be emitted. Aerosols containing chromic acid can be produced during the chrome-plating process; chromate is also the form found in air contaminated with cooling-tower drift.

7.3.3 Distribution in Soil

The chromium concentration in soil depends on geographic region, age of soil, and underlying parent rock material. Total chromium content within most soils (Tables 7.13 and 7.14) ranged from <5 ppm chromium to about 1000 ppm, although most soils contain <300 ppm (Swaine, 1955). In a detailed study of element composition in U.S. surficial soils, Shacklette et al. (1971) found that 64% of the soil samples contained total chromium concentrations in the range of 25 to 85 ppm (Figure 7.3). In general, the clay fraction of soil contains a higher chromium concentration than do other soil components (Tables 7.14 and 7.15).

Table 7.13. Chromium content of soils in various countries

Location	Number of samples	Chromium content (ppm)	Remarks
Canada			
Quebec	5	Found	Surface and subsoil
Cook Islands			
Atiu, Mangaia, and Aitutaki	3 surface	500-1,650 (1,250)[a]	Total
	3 subsoil	550-1,150 (900)	
Lower Cook Islands	8 surface	600-1,650 (1,100)	Total; two profiles; derived from basalt
	5 subsoil	550-1,570 (920)	
Mangaia, Atiu, and Mauke	4 surface	500-900 (750)	Total; derived from basalt alluvium mixed with limestone
	1 subsoil	550	
Cuba	Surface Subsoil	400-21,500	Mean total values for six important soil types
	11 surface	1,300-11,600 (3,900)	Total; four profiles; representative soils
	16 subsoil	<350-21,500 (4,500)	
	3 surface	350-24,600 (15,400)	Total; one profile; infertile soils derived from rocks high in Mg, Cr, and Ni
	2 subsoil	2,900, 23,900	
Czechoslovakia			
Mohelno, Bohemia	10 surface	685-1,700 (1,245)	Total; five profiles; derived from serpentine
	10 subsoil	860-2,135 (1,355)	
Moravia, northwest Bohemia		Found	Various parent materials
	1 surface	1,830	Total; one profile; forest soil derived from serpentine; pines showed stunted growth
	4 subsoil	1,040-2,050 (1,620)	
	1 surface	3.9	Extract 1% citric acid; one profile; forest soil derived from serpentine; pines showed stunted growth
	4 subsoil	2.9-4.0 (3.5)	
Dominican Republic			
Sierra de Bahoruco	1	700	Composite sample; aluminous lateritic soil
Finland		<100	From peat bogs (some near ores)
France	16 surface	2-87 (30)	Different types
	2 subsoil	56, 88	
	34 surface	1.8-114 (44)	Fused Na_2CO_3-KNO_3; total; two profiles
	8 subsoil	16-64	

Table 7.13 (continued)

Location	Number of samples	Chromium content (ppm)	Remarks
Germany			
Baden	13 surface	90-122 (107)	Fused Na_2O_2-NaOH; total; three profiles; different types; various parent materials
	12 subsoil	73-138 (107)	
	16 surface	47-108 (85)	Fused $NaHSO_4$; 15 profiles; different types; various parent materials
	31 subsoil	62-122 (87)	
Haiti			
Rochelois Plateau	1	550	Composite sample; aluminous lateritic soil
New Caledonia	1 surface	33,500	Total; one profile; derived from serpentine
	2 subsoil	20,900, 21,400	
	1 surface	4.5	Exchangeable; derived from serpentine
New Zealand			
North Auckland	4 surface	350-550 (500)	Ironstone soils; mostly on basalt
	1 subsoil	500	
Niue Island	3 surface	1,150-1,500 (1,300)	Total
	2 surface	400, 400	Soluble in 2.1% HCl
Puerto Rico	5 surface	7,950-8,650 (8,450)	Total; unproductive; laterites derived from serpentine
Near Mayaguez	1 surface	26,400	Total; Nipe clay profile; derived from serpentine
	4 subsoil	21,700-35,800 (26,100)	
	4 surface	750-26,400 (11,600)	Total; one profile; infertile soils derived from rocks high in Mg, Cr, and Ni
	5 subsoil	21,800-35,800 (27,200)	
	3 surface	0.2-0.6 (0.4)	Extract neutral 1 *N* NH_4Ac; infertile soils derived from rocks high in Mg, Cr, and Ni
Russia			
Along 40th meridian		(approx) 50	Zonal soils of the Russian plain
Various parts	15 surface	29-570 (241)	13 profiles; different types
	35 subsoil	5-760 (195)	
Scotland			
Near Huntly	1 surface	145	Total; profile formed from basic rocks
	7 subsoil	154-321 (234)	
Northeast	2	1,720, 2,890	Total; derived from serpentine
	Surface	10-5,000	Total
	3	0.11-0.17 (0.14)	Extract 2.5% HAc; derived from granite, norite, or old red sandstone
	41 surface	15-500 (140)	Total; 34 profiles; cultivated, uncultivated; different parent materials
	110 subsoil	200-800 (210)	
	20 surface	<0.02-0.56 (0.16)	Extract 0.5 *N* HAc; 17 profiles; cultivated, uncultivated; different parent materials
	66 subsoil	<0.02-0.66 (0.18)	
	16 surface	<0.01-0.10 (0.02)	Extract 1 *N* NH_4Ac, pH 7; 14 profiles; cultivated, uncultivated; different parent materials
	53 subsoil	<0.01-0.07 (0.01)	
	5 surface	<0.02-0.06 (0.02)	Extract 1 *N* NH_4Ac, pH 8.5; four profiles; cultivated, uncultivated; different parent materials
	17	<0.01-0.03 (<0.01)	

Table 7.13 (continued)

Location	Number of samples	Chromium content (ppm)	Remarks
North	6	5-700 (185)	Total; cultivated; different parent materials
Aberdeenshire	2 surface	3,000, 3,500	Total; two profiles; cultivated; on serpentine till
	8 subsoil	2,000-3,000 (2,500)	
	2 surface	0.69, 2.1	Extract 0.1 *N* HCl; two profiles; cultivated; on granite till and basic igneous till
	8 subsoil	0.10-3.2 (1.3)	
	2 surface	0.02, 0.05	Extract 0.0025 *N* HCl; two profiles; cultivated; on granite till and basic igneous till
	8 subsoil	<0.02-0.12 (0.05)	
Aberdeenshire	1 surface	0.33	Extract 0.5 *N* HAc; one profile; cultivated; on serpentine till
	4 subsoil	0.39-1.1 (0.68)	
Whitecairns, Aberdeenshire	4 surface	0.39-0.76 (0.60)	Extract 2.5% HAc; serpentine parent material; cultivated
Solomon Islands			
Siota, Gela	1 surface	8,000	Total; laterite
	1 surface	450	Soluble in 21% HCl; laterite
	1 surface	0.1	Exchangeable; laterite
South Africa		1,400-2,700	Treated HF-H_2SO_4 and fused $K_2S_2O_7$; total; derived from chromiferous rocks of Bushveld igneous complex
Transvaal		Detected	Chromite present; citrus-growing area
Sweden			
Near Uppsala and Stockholm	8	3-30 (8)	Each a composite of at least 20 cultivated post-glacial clays
United States			
Hawaiian Islands	11 surface	400-1,800 (900)	Total; six profiles; different types; derived from lava or volcanic ash
	23 subsoil	250-1,850 (800)	
Hyde Swamps, N.C.	3	195-245 (225)	Total on ash; about 2% ash; peat
Pennsylvania	1 surface	14	Total
	1 subsoil	14	
Various parts	13 surface	<15-125 (50)	Total; different parent materials
	13 subsoil	15-170 (65)	
	16 surface	"None"-16,200 (2,800)	Total; 12 profiles; infertile soils derived from rocks high in Mg, Cr, and Ni
	24 subsoil	"None"-4,600 (1,300)	
	11 surface	0.3-2.0 (0.7)	Extract neutral 1 *N* NH_4Ac; infertile soils derived from rocks high in Mg, Cr, and Ni
	14 surface	4-62 (16)	Heated H_2SO_4, HBr + Br_2; probably total; 11 profiles
	44 subsoil	0-34 (11)	
Peninsular Florida	77 surface	<1-300 (approx 40)	Cultivated, virgin; samples ignited at 450°C
	55 subsoil	<1-1,000 (approx 60)	
Florida	2 surface	30,300	Two profiles; everglades peat and Okeechobee muck
	16 subsoil	<1-100	
	9 surface	<10-500	Citrus soils; samples ignited at 450°C
Western Samoa	5 surface	950-3,350 (1,900)	Total; five profiles; laterites
	11 subsoil	900-2,350 (1,600)	
Vaitele and Savaii	2 surface	1,100, 1,650	Total; laterites
	2 subsoil	1,250, 1,800	
	1 surface	250	Soluble in 21% HCl; laterites
	2 subsoil	400, 400	

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[a] Average chromium content.

Source: Adapted from Swaine, 1955, pp. 29-34. Reprinted by permission of the publisher.

Table 7.14. Chromium concentrations in selected soils (ppm)

Material	Total soil chromium concentration	Reference
Soil, on road	71	Conner et al., 1971
Soil, off road	71	Conner et al., 1971
Soil	36.1 ± 0.2	Andersson and Nilsson, 1972
Soil	47	Shimp et al., 1957
Clay	157	Shimp et al., 1957
Annandale loam	32	Prince, 1957
Collington sandy loam	20	Prince, 1957
Coltz loam	40	Prince, 1957
Cossayuna loam	20	Prince, 1957
Croton silt loam	38	Prince, 1957
Lansdale loam	30	Prince, 1957
Norton loam	75	Prince, 1957
Sassafras sandy loam	45	Prince, 1957
Squires loam	46	Prince, 1957
Washington loam	39	Prince, 1957
Umiat bentonite	6.4	Murrmann, Winters, and Martin, 1971
Kaolinite-7	48.1	Murrmann, Winters, and Martin, 1971
Illite-35	79.0	Murrmann, Winters, and Martin, 1971
Fairbanks silt	280	Murrmann, Winters, and Martin, 1971
Barrow silt	126	Murrmann, Winters, and Martin, 1971
Suffield silt	6.4	Murrmann, Winters, and Martin, 1971
Surface soil		
Residential area	3.2 ± 3.3	Klein, 1972
Agricultural area	4.6 ± 3.6	Klein, 1972
Industrial area	8.5 ± 9.0	Klein, 1972
Airport	17.6 ± 8.9	Klein, 1972
Calcareous soil	130–150	Proctor, 1971
Muck soil	12–46	Chattopadhyay and Jervis, 1974
Soil in England	1.8–110	Cawse, 1974

Table 7.13 (continued)

Location	Number of samples	Chromium content (ppm)	Remarks
North	6	5-700 (185)	Total; cultivated; different parent materials
Aberdeenshire	2 surface	3,000, 3,500	Total; two profiles; cultivated; on serpentine till
	8 subsoil	2,000-3,000 (2,500)	
	2 surface	0.69, 2.1	Extract 0.1 *N* HCl; two profiles; cultivated; on granite till and basic igneous till
	8 subsoil	0.10-3.2 (1.3)	
	2 surface	0.02, 0.05	Extract 0.0025 *N* HCl; two profiles; cultivated; on granite till and basic igneous till
	8 subsoil	<0.02-0.12 (0.05)	
Aberdeenshire	1 surface	0.33	Extract 0.5 *N* HAc; one profile; cultivated; on serpentine till
	4 subsoil	0.39-1.1 (0.68)	
Whitecairns, Aberdeenshire	4 surface	0.39-0.76 (0.60)	Extract 2.5% HAc; serpentine parent material; cultivated
Solomon Islands			
Siota, Gela	1 surface	8,000	Total; laterite
	1 surface	450	Soluble in 21% HCl; laterite
	1 surface	0.1	Exchangeable; laterite
South Africa		1,400-2,700	Treated HF-H_2SO_4 and fused $K_2S_2O_7$; total; derived from chromiferous rocks of Bushveld igneous complex
Transvaal		Detected	Chromite present; citrus-growing area
Sweden			
Near Uppsala and Stockholm	8	3-30 (8)	Each a composite of at least 20 cultivated post-glacial clays
United States			
Hawaiian Islands	11 surface	400-1,800 (900)	Total; six profiles; different types; derived from lava or volcanic ash
	23 subsoil	250-1,850 (800)	
Hyde Swamps, N.C.	3	195-245 (225)	Total on ash; about 2% ash; peat
Pennsylvania	1 surface	14	Total
	1 subsoil	14	
Various parts	13 surface	<15-125 (50)	Total; different parent materials
	13 subsoil	15-170 (65)	
	16 surface	"None"-16,200 (2,800)	Total; 12 profiles; infertile soils derived from rocks high in Mg, Cr, and Ni
	24 subsoil	"None"-4,600 (1,300)	
	11 surface	0.3-2.0 (0.7)	Extract neutral 1 *N* NH_4Ac; infertile soils derived from rocks high in Mg, Cr, and Ni
	14 surface	4-62 (16)	Heated H_2SO_4, HBr + Br_2; probably total; 11 profiles
	44 subsoil	0-34 (11)	
Peninsular Florida	77 surface	<1-300 (approx 40)	Cultivated, virgin; samples ignited at 450°C
	55 subsoil	<1-1,000 (approx 60)	
Florida	2 surface	30,300	Two profiles; everglades peat and Okeechobee muck
	16 subsoil	<1-100	
	9 surface	<10-500	Citrus soils; samples ignited at 450°C
Western Samoa	5 surface	950-3,350 (1,900)	Total; five profiles; laterites
	11 subsoil	900-2,350 (1,600)	
Vaitele and Savaii	2 surface	1,100, 1,650	Total; laterites
	2 subsoil	1,250, 1,800	
	1 surface	250	Soluble in 21% HCl; laterites
	2 subsoil	400, 400	

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[a] Average chromium content.

Source: Adapted from Swaine, 1955, pp. 29-34. Reprinted by permission of the publisher.

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Material	Total soil chromium concentration	Reference
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Coltz loam	40	Prince, 1957
Cossayuna loam	20	Prince, 1957
Croton silt loam	38	Prince, 1957
Lansdale loam	30	Prince, 1957
Norton loam	75	Prince, 1957
Sassafras sandy loam	45	Prince, 1957
Squires loam	46	Prince, 1957
Washington loam	39	Prince, 1957
Umiat bentonite	6.4	Murrmann, Winters, and Martin, 1971
Kaolinite-7	48.1	Murrmann, Winters, and Martin, 1971
Illite-35	79.0	Murrmann, Winters, and Martin, 1971
Fairbanks silt	280	Murrmann, Winters, and Martin, 1971
Barrow silt	126	Murrmann, Winters, and Martin, 1971
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Surface soil		
Residential area	3.2 ± 3.3	Klein, 1972
Agricultural area	4.6 ± 3.6	Klein, 1972
Industrial area	8.5 ± 9.0	Klein, 1972
Airport	17.6 ± 8.9	Klein, 1972
Calcareous soil	130-150	Proctor, 1971
Muck soil	12-46	Chattopadhyay and Jervis, 1974
Soil in England	1.8-110	Cawse, 1974

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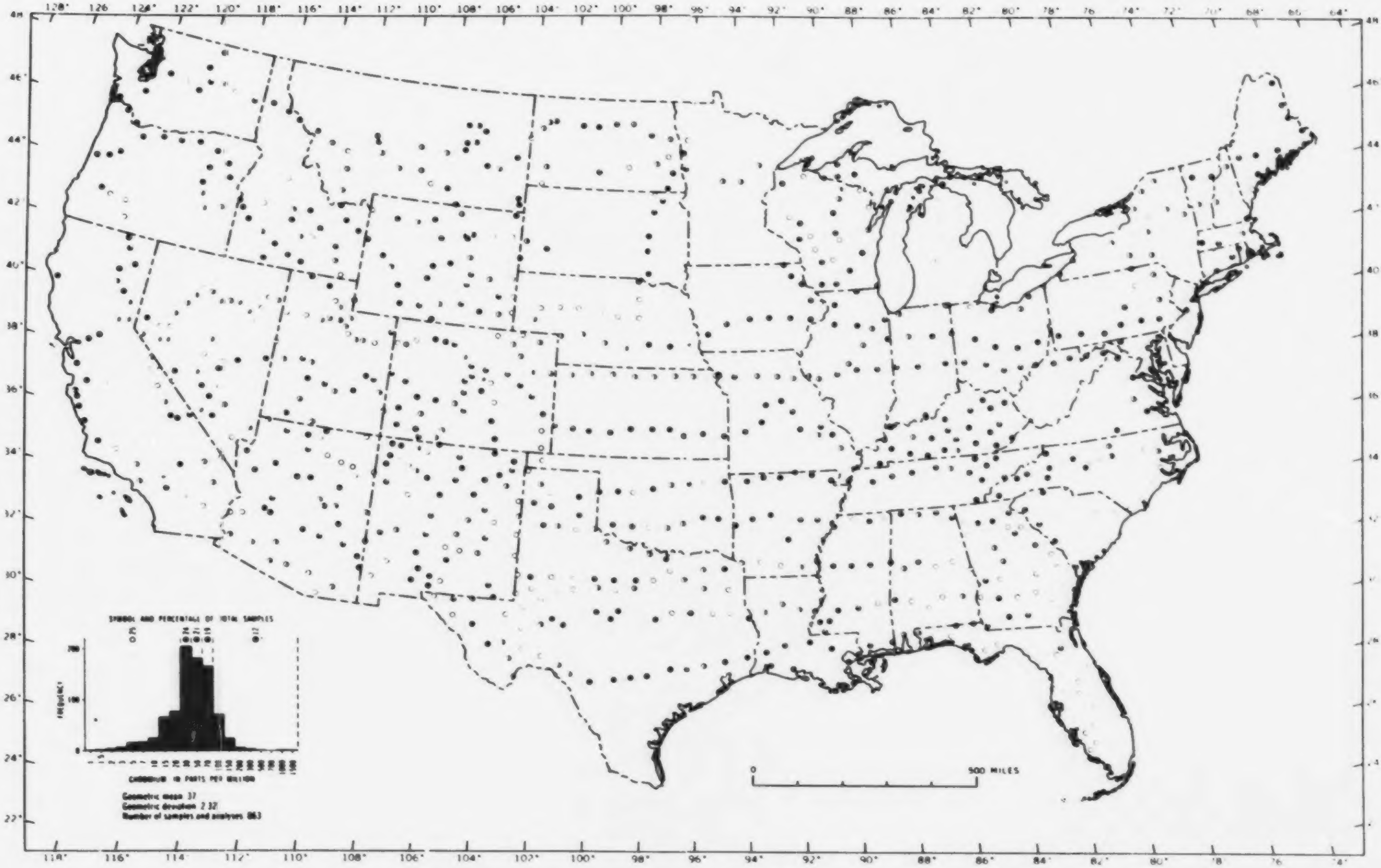
SYMBOL AND PERCENTAGE OF TOTAL SAMPLES
FREQUENCY
200
100
0
CHROMIUM IN PARTS PER MILLION
Geometric mean 37
Geometric deviation 2.32
Number of samples and analyses 863
0
500 MILES

Figure 7.3. Chromium content of U.S. surficial materials. Source: Shacklette et al., 1971, Figure 8, pp. D-24 - D-25.

Table 7.15. Chromium content of air-dried soils

Soil	Horizon	Soil depth		Chromium concentration (ppm)		
		(cm)	(in.)	Total	Extracted by neutral ammonium acetate	Extracted by 2.5% acetic acid
Brown podzol, freely drained on serpentine till	Surface	5.1-17.8	2-7	3500	0.10	0.31
	B_2	20.3-30.5	8-12	2000	0.04	1.10
	B_2	45.7-55.9	18-22	2000	0.01	0.39
	B-C	66.0-76.2	26-30	3000	0.01	0.60
	C	96.5-109.2	38-43	3000	0.01	0.63
Brown podzolic with gleyed B- and C-horizons imperfectly drained, on olivine gabbro till	Surface	0-20.3	0-8	300		
	B_2	30.5-38.1	12-15	100		
	B_3	40.6-48.3	16-19	200		
	B_3	50.8-61.0	20-24	300		
	C	91.4-111.8	36-44	300		
Brown forest soil freely drained on andesitic moraine	Surface	2.5-17.8	1-7	80		
	B_2	25.4-35.6	10-14	60		
	B-C	45.7-66.0	18-26	40		
	C	73.7-83.8	29-33	150		
Peaty gleyed podzol on granitic till	H	17.8-22.9	7-9	7		
	A_2	25.4-35.6	10-14	25		
	A_2	43.2-53.3	17-21	30		
	B_1	53.3	21	50		
	B_2	53.3-63.5	21-25	30		
	B_2-C	78.7-91.4	31-36	20		
	C	101.6-116.8	0-46	20		
Podzol, freely drained on granitic gneiss till	Surface	0-25.4	0-10	200	0.01	0.15
	B_2	30.5-35.6	12-14	150	0.01	0.08
	B_2	40.6-50.8	16-20	150	<0.01	0.11
	B_3	61.0-76.2	24-30	150	<0.01	0.08
	C	94.0-104.1	37-41	200	<0.01	0.11
Podzol, freely drained on quartz mica schist till	Surface	0-17.8	0-7	150		
	B_2	33.0-48.3	13-19	150		
	B_2	61.0-68.6	24-27	150		
	B_3	81.3-96.5	32-38	150		
	C	101.6-116.8	40-43	200		
Noncalcareous gley, poorly drained on Silurian slate till	A_1	5.1-12.7	2-5	250		
	A_2	12.7-22.9	5-9	250		
	B_2	27.9-35.6	11-14	250		
	B_2	40.6-50.8	16-20	200		
	B_3	61.0-76.2	24-30	200		
	C	91.4-106.7	36-42	200		
Peaty podzol with iron pan freely drained below pan on sandstone till	A_2	2.5-5.1	1-2	20		
	B_2	12.7-35.6	5-14	30		
	B_3	55.9-68.6	22-27	25		
	C	88.9-101.6	35-40	10		

Source: Adapted from Swaine and Mitchell, 196[illegible], Table 1, pp. 350-353 and Table 2, pp. 357-358. Reprinted by permission of the publisher.

Soils formed on serpentine rock have much higher total chromium concentrations than other soils (Table 7.13). Proctor (1971) found that total chromium concentrations ranged from 2500 to 4000 ppm (ash wt) for British and Swedish serpentine soils, and Lyon et al. (1970) found extreme variability in concentrations for serpentine regions of New Zealand (500 to 62,000 ppm, ash wt basis).

The chromium content at different soil depths has not been studied to any great extent. For Papua-New Guinea soils (serpentine) mean concentrations for horizons A_1, A_2, AB_1/B_1, AB_2/B_2. B_3/BC, and C_1 were 946, 970, 771, 396, 677, and 294 ppm, respectively (Bleeker and Austin, 1970). Chromium content of the parent material was 283 ppm. Chromium concentration was not correlated with clay content in these soils but was correlated with sand content, especially in the 50- to 75-μm and 150- to 210-μm fractions. Swaine and Mitchell (1960) reported total and extractable chromium concentrations for soils derived from different rock materials (Table 7.15). Content was similar in all three horizons. Chromium analyses of A-, B-, and C-horizons of podzol, Squires, Annandale, Wethersfield, and Norton soils and of their respective clay fractions (Table 7.16) showed that total chromium content did not differ significantly with depth (Conner, Shimp, and Tedrow, 1957). In a muck soil, total chromium concentrations were 12.1 to 14.3 ppm at the surface, 18.5 ppm at 0 to 7.5 cm, 30.2 ppm at 7.5 to 15.0 cm, 35.4 ppm at 15.0 to 22.5 cm, 45.8 ppm at 22.5 to 30.0 cm, 28.6 ppm at 30.0 to 37.5 cm, and 26.7 ppm at 37.5 to 45.0 cm (Chattopadhyay and Jervis, 1974).

Table 7.16. Chromium content of various soils and their clay fractions

Soil	Horizon	Chromium content (ppm)	
		Total soil	Clay fraction
Podzol on Wisconsin drift	A	17	101
	B	48	177
	C	43	140
Podzol on Kansan drift	A	12	81
	B	44	102
	C	51	160
Squires (derived from calcareous materials)	A	22	83
	B	7	108
	C	8	94
Annandale (derived from calcareous materials)	A	28	43
	B	30	34
	C	8	31
Wethersfield (derived from acid red shale)	A	10	134
	B	18	134
	C	21	167
Norton (derived from acid red shale)	A	20	167
	B	15	157
	C	33	164

Source: Adapted from Connor, Shimp, and Tedrow, 1957, Table 2, pp. 67-68. Reprinted by permission of the publisher.

The important consideration, however, is not total chromium but rather the chromium available for plant uptake; few studies have reported this value. Bradford, Blair, and Hunsaker (1971) found water-extractable chromium in only 8 of 68 California soil samples, with a mean chromium concentration of 0.01 ppm and a range of 0.01 to 0.017 ppm. For Lassen Adobe Clay, the pH of the water did not alter the amount of chromium extracted; <0.01 ppm was extracted at pH values of 3.9, 5.1, 6.7, and 7.6.

Swaine and Mitchell (1960) and Mitchell (1971) also reported a very low extractable (by 2.5% acetic acid) chromium content from a variety of soils even though the total chromium concentration was quite high in certain soils (Tables 7.15 and 7.17). Mortvedt and Giordano (1975) found that the amounts of chromium extractable with 0.1 *N* HCl from soils amended with different amounts of phosphate fertilizer were near their analytical detection limit (0.05 ppm) in most cases.

The total soil chromium concentration in the vicinity of a cooling tower decreased with distance from the pollution source; background levels were reached at a distance of about 300 m (Taylor et al., 1975) (Table 7.18). In the immediate vicinity of the cooling tower (15 and 60 m), total chromium concentrations were high at both 0- to 1-cm and 1- to 6-cm depths; however, in all cases, extractable chromium (by ammonium acetate, pH 4.8) was less than 6% of the total. Mean extractable concentrations from control regions and regions with near background levels for total chromium were in the range of 0.40 to 1.90 ppm.

In lysimeter experiments, Lehman and Wilson (1971) detected no measurable chromium extracted by sodium acetate from soils before or after application of sewage wastewater effluent.

Certain authors have characterized some soils as chromium deficient, where deficiency is defined as available chromium being below a level needed by the plant. Although chromium has not been shown to be essential for plants (Section 4.2.1), reports of increased crop yields following application of chromium to soils have suggested that a certain level of available chromium is needed for optimal plant growth and that some soils are deficient in this respect (Mertz, 1969). However, until various indirect effects are excluded and chromium is shown to be essential, such observations merely illustrate a beneficial effect from application of chromium compounds to soils.

In most cases, the chemical form of chromium within soil is a matter of conjecture, depending on parent rock material, anthropogenic input into soil, pH, and oxidizing conditions of soil. Since the major mineral form of chromium is chromite, a portion of chromium within soils, especially serpentine soils, is in this form. The majority of other mineral forms of chromium are rather inert and only sparingly soluble. During weathering of rocks, some solubilization of chromium can occur. With intensive oxidation, chromium(III) can be converted into the soluble chromate ion, CrO_4^{2-}, which can be precipitated by certain heavy metals such as lead (Goldschmidt, 1954). This oxidation probably rarely occurs in soils. Anthropogenic input of chromium is often as the CrO_4^{2-} ion, although it is usually initially discharged into waters. Because chromium(VI) is a strong oxidizing agent, it is usually converted to chromium(III), especially in the presence of organic matter. No data giving relative amounts of chromium(III) and chromium(VI) in soils were found. Chromium(III) tends to form six-coordinate octahedral complexes and in many cases probably precipitates as $Cr_2O_3 \bullet nH_2O$ (Section 2.2.3). Precipitation would increase with an increase in pH. The behavior of chromium(III) ions in soil has not been reported in any detail in the literature. In chromium clays (artificially constructed by adding

Table 7.17. Total and extractable chromium from nonserpentine and serpentine soils

Soil	Depth		Horizon	Chromium concentration (ppm dry wt)	
	(mm)	(in.)		Total	Extracted by 2.5% acetic acid
Peaty podzol on felsitic laval till[a]	25-50	1-2	F	5	0.04
	100-200	4-8	H	8	0.06
	255-330	10-13	A_1, A_2	80	0.53
	330	13	B_1, pan	80	0.83
	330-430	13-17	B_2	100	0.68
	610-710	24-28	B_3	100	0.34
Freely drained brown podzol on serpentine till	50-175	2-7	Surface	3500	0.31
	200-305	8-12	B_1	2000	1.10
	450-560	18-22	B_2	2000	0.39
	670-760	26-30	B_2-C	3000	0.60
	965-1090	38-43	C	3000	0.63

[a] Chromium content of vegetation on this soil was 1.3 ppm.

Source: Adapted from Mitchell, 1971, Table 4, p. 12 and Table 5, p. 13. Reprinted by permission of the Controller of Her Britannic Majesty's Stationery Office.

Table 7.18. Total and extractable chromium in soils exposed to cooling-tower drift

Distance from cooling tower (m)	0- to 1-cm soil depth			1- to 6-cm soil depth		
	Total[a] chromium (ppm)[c]	Extractable[b] chromium (ppm)[c]	Percent extractable	Total[a] chromium (ppm)[c]	Extractable[b] chromium (ppm)[c]	Percent extractable
15	458 ± 150	26.99 ± 4.74	5.89	267 ± 135	11.36 ± 2.91	4.25
60	172 ± 23	8.34 ± 1.52	4.84	108 ± 13	4.05 ± 0.37	3.75
180	67 ± 4	3.17 ± 0.78	4.73	70 ± 6	3.03 ± 1.0	4.32
300	53 ± 4	0.65 ± 0.15	1.22	50 ± 4	0.46 ± 0.11	0.92
600	53 ± 5	0.81 ± 0.17	1.52	54 ± 5	0.40 ± 0.12	0.74
900	52 ± 6	1.38 ± 0.6	2.65	46 ± 6	0.89 ± 0.31	1.93
1200	50 ± 5	1.61 ± 0.95	3.22	52 ± 6	1.90 ± 0.94	3.65
1500	39 ± 9	1.50 ± 0.72	3.84	56 ± 12	1.40 ± 0.83	2.51
1800	52 ± 6	0.43 ± 0.02	0.82	53 ± 6	0.45 ± 0.02	0.84
Control	50 ± 5	0.49 ± 0.01	0.98	58 ± 2	0.59 ± 0.06	1.01

[a] Total analyses determined by neutron activation techniques.

[b] Extracted in 1 *N* ammonium acetate adjusted to pH 4.8.

[c] Concentration in ppm ± 1 standard error.

Source: Adapted from Taylor et al., 1975, Table 1, p. 419.

0.5 *N* $Cr_2(SO_4)_3$ to montmorillonite clay and centrifuging), release of chromium by monovalent cations was relatively small compared to release of cobalt and nickel from their respectively constructed clays (Basu and Mukherjee, 1965). The order of ions arranged according to their ability to release increasing amounts of chromium from chromium clay was Al > Mg > NH_4 > K > Na. The sequence of exchange of H from a formulated H-clay was Cr >> Ni ≥ Co. Thus, chromium appears to be bound more tightly to montmorillonite clays than are either cobalt or nickel. Adsorbtion to clays, therefore, would decrease the soluble trivalent chromium content in the soil. This adsorption would increase at higher pH values (>6.0). Chromium ions could also adsorb to organic matter or form insoluble organometallic precipitates. No data were found on the importance of organic material in decreasing soluble chromium concentrations within soils.

In summary, while total chromium in soil varies, ranging up to 300 ppm in nonserpentine areas and to 1 to 2 wt % in serpentine soils, extractable chromium amounts are usually low (0.01 to 4.0 ppm) (Murrmann and Koutz, 1972). Most chromium in soil is apparently insoluble and, therefore, is not readily available for plant uptake.

7.3.4 Distribution in Water

Chromium, like a variety of other trace metals, can be found in both surface water and groundwaters in trace quantities (Table 7.19); the amount is usually related to anthropogenic input. This relationship can be most easily seen for stream and river water. No chromium was detected in 65 samples from California streams (Silvey, 1967), but 1250 ppb chromium was once detected in a contaminated stream in Nassau County, New York (Lieber, Perlmutter, and Frauenthal, 1964). A discussion of the problem of plating and sewage wastes contributing to this contamination in Nassau County can be found in Perlmutter and Lieber (1970). Abatement procedures have led to

Table 7.19. Concentration of chromium in water supplies

Water sample	Frequency of detection	Chromium concentration (ppb)		Reference
		Average	Range	
Lake Tahoe, Nev. area				
Tahoe City		<0.07		Bond, Straub, and Prober, 1973
Upper Truckee River		<0.71		Bond, Straub, and Prober, 1973
Trout Creek		<0.91		Bond, Straub, and Prober, 1973
Logan Creek		<0.71		Bond, Straub, and Prober, 1973
Incline Creek		<0.71		Bond, Straub, and Prober, 1973
Colorado River	12%		10-30	Bond, Straub, and Prober, 1973
Columbia River	87%		1-10	Bond, Straub, and Prober, 1973
Mississippi River	23%		3-20	Bond, Straub, and Prober, 1973
Missouri River	10%		8-10	Bond, Straub, and Prober, 1973
Ohio River	20%		4-10	Bond, Straub, and Prober, 1973
Oak Ridge, Tenn.				
Natural waters			50-120	Crosmun and Mueller, 1975
Waters near cooling tower			2500-2790	Crosmun and Mueller, 1975
U.S. surface waters	25%	<1	<1-19	Durum and Hem, 1972
U.S. surface waters	24.5%	9.7	1-112	Kopp, 1969
New York City area				
Uncontaminated stream		<10		Lieber, Perlmutter, and Frauenthal, 1964
Contaminated stream		1250		Lieber, Perlmutter, and Frauenthal, 1964
Uncontaminated well		<10		Lieber, Perlmutter, and Frauenthal, 1964
Contaminated well		6000		Lieber, Perlmutter, and Frauenthal, 1964
Illinois River		21	5-38	Mathis and Cummings, 1973
California				
Spring water	4 of 72 samples		0-21	Silvey, 1967
Well water	3 of 63 samples		0-13	Silvey, 1967
Stream water	0 of 65 samples			Silvey, 1967
Seawater	0 of 24 samples			Silvey, 1967
U.S. water supplies (2595 samples)		2.3	0-79	Soukup, 1972
Rhine River, Germany		18		De Groot and Allersma, 1973
Qishon River, Israel		<10		Kronfeld and Navrot, 1974
Poland				
Biala Przemsza			12-100	Pasternak, 1973
Sztola			6-44	Pasternak, 1973
Wisla			31-112	Pasternak, 1973
Seawater			0.04-0.07	Krauskopf, 1956

significant decreases in hexavalent chromium in the aquifer. Major industrialized rivers have variable chromium contents. A range of 5 to 38 ppb was reported in the Illinois River (Mathis and Cummings, 1973), 3 to 20 ppb in the Mississippi River (detection in 23% of samples), and 8 to 10 ppb in the Missouri River (detection in 10% of samples) (Bond, Straub, and Prober, 1973).

In a five-year study of trace element content in U.S. waters, Kopp and Kroner (1967) reported that dissolved chromium concentrations ranged from 0 to 112 ppb with a mean content of 9.7 ppb (Table 7.20). Concentrations

Table 7.20. Chromium in waters of the United States

Basin	Number of positive occurrences	Frequency of detection (%)	Chromium concentration (ppb)		
			Minimum	Maximum	Mean
Northeast	51	56	1	112	14
North Atlantic	36	21	1	29	6
Southeast	37	41	1	22	4
Ohio River	57	24	1	36	7
Lake Erie	11	23	6	25	12
Upper Mississippi River	20	18	1	20	7
Tennessee River	32	47	2	20	6
Western Great Lakes	19	29	1	20	6
Missouri River	3	17	1	7	3
Lower Mississippi River	31	20	2	90	16
Colorado River	17	17	3	63	16
Western Gulf	3	6	5	56	25
Pacific Northwest	53	33	1	36	6
California	6	21	2	45	15
Summary	386	25	1	112	9.7

Source: Compiled from Kopp and Kroner, 1967.

were apparently related to industrial activity. For example, samples from Lake Michigan near Milwaukee, Wisconsin, contained chromium in two of ten samples (2 and 4 ppb), while in Lake Michigan near Gary, Indiana, an area with greater industrial discharges, water contained chromium in three of nine samples (5 to 19 ppb). Although not as completely analyzed, chromium was found in suspended matter in 8% of the samples (18 of 288 samples), with a mean chromium concentration of 30 ppb in water. The Northeast basin had the largest frequency of detection. In an earlier study, Durum and Haffty (1963) reported a range of 0.72 to 84 ppb chromium in rivers, with Atlantic coastal rivers having "slightly enriched" concentrations compared to the average for all U.S. streams.

Chromium concentrations in seawater are very low; no chromium was detected in 24 samples from off the California coast (Silvey, 1967), and a range of 0.5 to 0.25 ppb chromium was reported in another study (Bond, Straub, and Prober, 1973).

In a tabulation of chromium concentrations in various waters used for water supply, river waters contained amounts ranging from undetectable to 7.8 ppb; lake waters from 0.34 to 2.8 ppb; impoundment waters from undetectable amounts to 3.8 ppb; and groundwaters, wells, and infiltration galleries from undetectable amounts to 1.1 ppb (Bond, Straub, and Prober, 1973).

In 1969, the Community Water Supply Survey (CWSS) found that hexavalent chromium concentrations in finished drinking water exceeded the Public Health Service's mandatory limit for drinking water (50 ppb) in four of the 969 public water supply systems examined (McCabe et al., 1970).

The suspended load (defined as being the material retained on a 0.45-μm filter) and the trace element composition of this suspended material has been determined in several U.S. rivers (Table 7.21). Analyses showed chromium concentrations in this material to range between 37 and 460 ppm on a dry weight basis (Turekian and Scott, 1967). Because most chromium compounds are insoluble and suspended matter in water has both cation-exchange capacity and adsorption properties and would therefore likely take up any soluble chromium, most chromium would probably be in particulate form. Chromium concentrations in dry-season suspended silts of southern California were approximately 500 ppm in "natural" areas and 2000 ppm in urbanized areas (Chen et al., 1974). Anthropogenic output of soluble chromates would account for a higher soluble chromium content in pollution outfalls; however, at low pH values in reducing situations, chromate would be reduced to Cr_2O_3 (Section 2.2.5). Chromate was not found to adsorb onto montmorillonite, illite, kaolinite, ferric oxide, manganese oxide, hydrated ferric oxide, or peat (Kharkar, Turekian, and Bertine, 1968). In the Walker Branch Stream, Walker Branch Watershed, Oak Ridge, Tennessee, 32.4% of the total chromium was in soluble form (six-month average) (Andren, Lindberg, and Bate, 1975).

Analysis of water from a Norwegian fjord showed that the chromium content in unfiltered water increased from about 0.56 ppm at a 1-m depth to about 1.7 ppb at a 180-m depth (Piper, 1971). At a 1-m depth, about 0.2 ppb chromium was in soluble form (passing through a 0.45-μm filter), whereas

Table 7.21. Chromium composition of suspended material in rivers

River	Suspended load (mg/liter)	Chromium content (ppm dry wt)
Brazos, Tex.	954	100
Colorado, Tex.	150	82
Red, La.	436	37
Mississippi, Ark.	185	150
Tombigbee, Ala.	25	220
Alabama, Ala.	54	150
Chattahoochie, Ga.	71	190
Flint, Ga.	12	210
Savannah, S. C.	30	460
Wateree, S. C.	37	200
Pee Dee, S. C.	188	150
Cape Fear, N. C.	61	130
Neuse, N. C.	36	380
Roanoke, N. C.	33	240
James, Va.	41	290
Rappahannock, Va.	28	140
Potomac, Va.	34	170
Susquehanna, Pa.	54	290
Rhone, France Avignon, June 1966	296	150
Rio Maipo, Chile Puente Alto, South of Santiago, September 1966	41	68

Source: Adapted from Turekian and Scott, 1967, Table I, p. 942. Reprinted by permission of the publisher.

about 0.26 ppb was in particulate form. At a 40-m depth, filtered water contained about 0.56 ppb chromium, while suspended chromium was only 0.04 ppb. Apparently, chromium was present as a hydroxide in the more shallow depths (pH 8.0, Eh 0.44 V) but solubilized at greater depths (pH 6.9). Although chromium(VI), a potent oxidizing agent, is usually reduced in the presence of organic matter, it can be retained in natural waters which contain low concentrations of reducing matter (Section 2.2.5).

The valence of chromium in seawater can be either six or three. Fukai (1967) suggested that the stable chromium species in seawater was chromium(VI), but provided data to show both forms were present. Surface seawater contained from 0.02 to 0.14 ppb chromium(III) and from 0.28 to 0.36 ppb chromium(VI), while seawater at depths of 5, 500, and 1000 m contained about 0.2 ppb chromium(III) and 0.2 ppb chromium(VI). Studies of ^{51}Cr release (initially as $Cr_2O_7^{2-}$) into the Columbia River at Hanford, Washington, have shown that most ^{51}Cr entering seawater remains hexavalent (as CrO_4^{2-}) and that any chromium(III) formed would usually be sorbed to sediment particles and removed from true solution (Cutshall, Johnson, and Osterberg, 1966).

7.3.5 Distribution in Sediments

Although chromium concentrations have been determined for a variety of sediments (Table 7.22), few detailed studies with depth of sediment, background level of chromium, chemical form of chromium, and relationship to pollution sources have been reported. Chromium content of Rhine River sediments ranged from a few parts per million to over 1200 ppm (De Groot and Allersma, 1973). Estimated background levels were between 20 and 40 ppm chromium for southern Lake Michigan (Leland, Shukla, and Shimp, 1974) and 64 ppm chromium in the Firth of Clyde Estuary (MacKay, Halcrow, and Thornton, 1972).

In the San Pedro, Santa Monica, Santa Barbara, and Soledad basins of California, chromium concentrations did not change to any great extent with depth (Figure 7.4) (Bruland et al., 1974). Chromium concentrations in the upper sediments increased slightly for the San Pedro and Santa Monica basins and decreased slightly in the Santa Barbara and Soledad basins. Background values for each basin are roughly 100 ppm chromium, assuming that little anthropogenic chromium deposition occurred before 1900.

The chromium concentration in sediments of several Wisconsin lakes did not significantly decrease with depth (Table 7.23) (Iskandar and Keeney, 1974). No reason was suggested for enrichment of surface layers in Lakes Mendota, Monona, and Waubesa. If sediments greater than 50-cm in depth are considered "precultural" in origin, then reasonable estimates for background levels of chromium in sediments would be from <1 to 35 ppm. Although quantitative estimates of the contributions from diverse transporting agencies were not possible, outfall wastes probably accounted for the chromium observed in the sediments.

Surface sediments of southern Lake Michigan contained an average of 77 ppm chromium (range of 35 to 165 ppm), while the 15- to 100-cm depth sediment contained 52 ppm chromium (range of 32 to 68 ppm) (Leland, Shukla, and Shimp, 1974). Although the significance of values was not stated, apparently chromium was not greatly increased in Lake Michigan sediments. The wider range in surface sediments, however, suggested that chromium has been deposited more sporadically in recent times. The chromium concentrations were more closely related to the organic carbon content of the surficial sediment than to clay particle size.

Other studies, however, suggested that chromium was accumulating in the upper 10 cm of lower Lake Michigan sediments. Gross et al. (1972) stated,

Table 7.22. Concentration of chromium in sediments

Sample area	Chromium concentration (ppm)		Reference
	Average	Range	
Delaware Bay		33-447	Bopp and Biggs, 1972
New York City Bight			
Background	106	2-310	Carmody, Pearce, and Yasso, 1973
Sludge dumping area	105	50-209	Carmody, Pearce, and Yasso, 1973
Puget Sound			
Seattle area		70-139	Crecelius, Bothner, and Carpenter, 1975
Tacoma area		43-154	Crecelius, Bothner, and Carpenter, 1975
Southern region		58-135	Crecelius, Bothner, and Carpenter, 1975
Hood Canal		80-126	Crecelius, Bothner, and Carpenter, 1975
Texas			
Houston ship channel		39-254	Hann and Slowey, 1972
Neches River		8-288	Hann and Slowey, 1972
Sabine River (low industrial activity)		41-89	Hann and Slowey, 1972
Southern Lake Michigan			
Surface sediments	77	35-165	Leland, Shukla, and Shimp, 1974
Sediments from >15- to 100-cm depth	52	32-68	Leland, Shukla, and Shimp, 1974
Estimated background		20-40	Leland, Shukla, and Shimp, 1974
Illinois			
Illinois River (Peoria)	17	2-87	Mathis and Cummings, 1973
Nonindustrial streams	6	3-7	Mathis and Cummings, 1973
Long Island Sound (mud)		190-450	Wogman, Rieck, and Kosorok, 1974
Buzzards Bay, Mass.	33		Mackay, Halcrow, and Thornton, 1972
Canada			
Ottawa River	22		Oliver, 1973
Rideau River	21		Oliver, 1973
Silt	27		Oliver, 1973
Medium-size particles	9		Oliver, 1973
Rhine River	1240		De Groot and Allersma, 1973
Meuse River	620		De Groot and Allersma, 1973
Scheldt River	380		De Groot and Allersma, 1973
Ems River	180		De Groot and Allersma, 1973
Chao Phya, Thailand	100		De Groot and Allersma, 1973
Tji Tarum, Java	40		De Groot and Allersma, 1973
Rotterdam Harbor			
Inner	868		De Groot and Allersma, 1973
Intermediate	434		De Groot and Allersma, 1973
Outer	186		De Groot and Allersma, 1973
Firth of Clyde			
Background	64 ± 20	38-106	Mackay, Halcrow, and Thornton, 1972
Sludge dumping area	164 ± 84	48-308	Mackay, Halcrow, and Thornton, 1972
Clyde Estuary	624		Mackay, Halcrow, and Thornton, 1972
Gulf of Paria, Trinidad	93		Mackay, Halcrow, and Thornton, 1972
Saanich Inlet, British Columbia	81		Mackay, Halcrow, and Thornton, 1972

"In many cores these accumulations are 5 to 20 times as great as concentrations of the same trace elements found 1 m deeper in the core." These chromium concentrations correlated best with concentrations of organic carbon.

In sediments of the Ottawa and Rideau rivers, Oliver (1973) observed a significant correlation between surface area of particles and their metal content. Silt (0.004 to 0.062 mm) contained 27 ppm chromium, while medium-sized particles (0.5 to 2.0 mm) contained 9 ppm. In Puget Sound sediments,

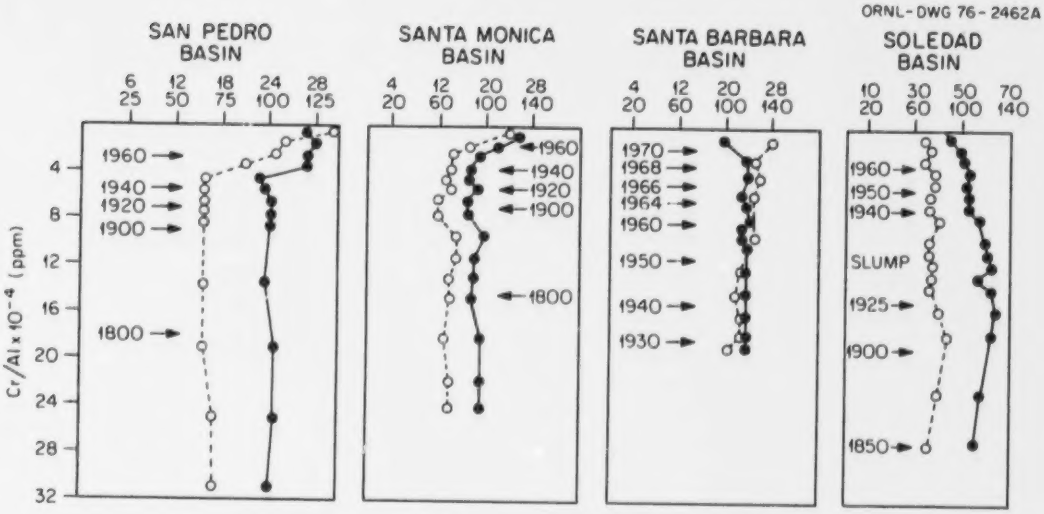

Figure 7.4. Chromium concentration in sediments from the southern California basins. Source: Adapted from Bruland et al., 1974, Figure 3, p. 426. Reprinted by permission of the publisher.

no elevated chromium levels attributable to input by man were observed (Crecelius, Bothner, and Carpenter, 1975). In addition, statistical analyses did not demonstrate a strong relationship between chromium concentrations and sediment grain size.

Site and rate of deposition of suspended matter carried by a river into a lake depends on many factors, such as area water turbulence and size of suspended particles. In Lake Michigan at Grand Haven, Michigan, Robbins and Edgington (1973) found that fine particles did not begin to settle for about a 6 mile distance, and then the prevailing north-south internal and wind-induced currents in the lake produced a north-south band of deposition in the sediments from 4 to 17 miles off the shoreline. Chromium concentrations in surface sediments were from about 100 to 180 ppm and from 60 to 180 ppm in samples from various depths (up to 20 cm). Deposition within a body of water, therefore, is not the same in all areas. Careful selection of sample sites and analysis of factors influencing deposition at these sites are necessary for a complete picture of metal accumulation within sediments.

7.4 ENVIRONMENTAL FATE

No comprehensive studies on the resident times or fate of chromium within the various media have been made. However, the few available reports presented enough data to identify some of the mechanisms involved in movement of chromium among the media. The most obvious lack of information is in the quantitative aspects of such movements and, of course, the actual amounts of each element would depend on the particular circumstances.

Table 7.23. Chromium concentration in sediments of Wisconsin lakes (ppm dry wt)

Lake	Depth (cm)						
	0-5	5-10	10-15	15-20	20-25	25-50	>50
				Northern Wisconsin lakes			
Mary	1	1	1.5		1.5	1.7	0.8
Tomahawk	28	18	20	17	20	26	16
Minocqua	4.2	4.0	4.8	3.9	2.0	33	5.4
Phillips	38	32	32	26	28	35	35
Butternut	26	19	21	23		35	
				Southern Wisconsin lakes			
Mendota	42	38	33		30	16	11
Monona	49	46	38	28	10	8	7
Waubesa	33	24	35	36	30	22	17
Kegonsa	17	13	16	18	18	15	15
Wingra	17	23	21	19		23	18

Source: Adapted from Iskandar and Keeney, 1974, Table III, p. 167. Reprinted by permission of the publisher.

7.4.1 Mobility and Persistence in Air

Chromium is removed from air by fallout and precipitation. In New York City, the average amount of chromium deposited monthly by precipitation was 0.15 μg/m², with a range of 0.05 to 0.25 μg/m² (Volchok and Bogen, 1973). The average chromium concentration in precipitation was 0.025 μg/ml with a range of 0.005 to 0.060 μg/ml over 11 months.

Cawse (1974) presented data on trace element contents of wet and dry deposition in the United Kingdom. Rainwater contained between 0.64 and 34 ppb chromium in rural England and 9.3 ppb in central Swansea (urban area). Total annual chromium deposition was between 0.12 and 1.9 μg/m² with dry deposition accounting for 0.023 to 0.44 μg/m². Depending upon locale, between 44% and 96% of total deposition occurred by wet precipitation. Although data for chromium are sparse and exhibit a considerable range of values, urban areas have somewhat higher wet and total deposition amounts than do rural areas. Concentrations of chromium in rainwater were 3.6 ppb for Heidelberg, Germany; 2 ppb for Quiltayute, Washington; and 2.9 ppb for Waymire, United Kingdom (Bogen, 1974).

At the Walker Branch Watershed, Oak Ridge, Tennessee, chromium concentrations in rainwater varied from 0.7 to 3.9 ppb over a 14-month period (Andren et al., 1974; Andren, Lindberg, and Bate, 1975). Monthly total amounts of chromium delivered to the watershed ranged from 0.6 to 10.7 g/ha, with a monthly average of 3.9 g/ha. From January to June 1974, monthly average rain deposition was 2.9 g/ha (range 0.6 to 8.4 g/ha), while dry deposition was 0.76 g/ha (range 0.16 to 2.18 g/ha). Apparently, most chromium is deposited on land by wet fall (rain or snow) and is obviously related to the amount of rain or snow occurring during the sampling period.

Rainfall ash contained 420 and 450 ppm chromium in two samples from England. These concentrations were higher than those in the fly ash released to the environment from the neighboring generating stations (Hallsworth and Adams, 1973). Thus, other unidentified sources contributed to the rainwater ash.

7.4.2 Mobility and Persistence in Soil

Few studies which presented data on the fate of chromium in soils were found. Most soil chromium is in mineral, adsorbed, or precipitate form and is not easily transported to other media. On the basis of correlation analysis, the chromium in aerosols over the San Francisco Bay area was shown to be largely derived from soil (John et al., 1973). Atmospheric chromium at the South Pole is probably derived partly from the ocean and partly from crustal weathering (Zoller, Gladney, and Duce, 1974). Thus, weathering and wind action can transport soil chromium to the atmosphere.

Chromium is also removed from soils by both runoff and by percolating water, but data on this type of removal are lacking. Runoff could remove both chromium ions and bulk precipitates of chromium, with final deposition on either a different land area or a body of water. In addition, flooding of soils and the subsequent anaerobic decomposition of plant matter may increase dissolution of metal oxides in the soil (Kee and Bloomfield, 1962). Rates of dissolution depend on the particular soil characteristics. For example, water extracted 0.5 ppm chromium and 2.5% acetic acid extracted 0.8 ppm chromium from a 17.5-cm (7-in.) layer of grassy soil incubated for 39 days under anaerobic conditions. Aerobic incubation of the same soil without grass for the same length of time resulted in 0.04 ppm chromium extracted by water and 0.4 ppm extracted by 2.5% acetic acid. Before incubation, water and 2.5% acetic acid extracted about 0.05 and 0.04 ppm chromium, respectively, from the grassy soil samples and 0.01 and 0 ppm chromium, respectively, from the soil without grass. Subsequent aeration of samples resulted in partial immobilization of the trace elements.

7.4.3 Mobility and Persistence in Water and Sediments

No experimental studies describing the fate of chromium within natural waters were found. Since most chromium in water is in particulate form, it would ultimately be deposited in sediments. Considerable amounts of material could be transported in flowing waters. The Susquehanna River transports approximately 790 metric tons of chromium per year (Turekian and Scott, 1967). The chromium input from natural streams into Lake Michigan is estimated to be about 30 metric tons per year; the input from air pollution is higher, approximately 90 metric tons per year (Winchester and Nifong, 1971).

Various physical forms of metals in streams can be transported by river current (Table 7.24) (Gibbs, 1973). The percentage transported in each form was determined for iron, nickel, cobalt, copper, chromium, and manganese and was different for each metal. Crystalline sediments were the major form of chromium transported in the two rivers studied. De Groot and Allersma (1973) found a metal-in-water to metal-in-suspended-matter ratio of 1 to 2.3 for the Rhine River. In the heavily polluted Qishon-Gadura River system in Israel, chromium concentrations in water were <10 ppb, while sediments in the contaminated region contained from 220 to 610 ppm chromium. Since this region of the river system has relatively high pH values (10 to 11), efficient removal of heavy metals from the water occurs. Even boiling water did not extract any chromium from these sediments. Dean, Bosqui, and Lanouette (1972) listed 5.3 as the pH above which most chromium(III) precipitates from dilute solutions.

Table 7.24. Chromium transported by five phases in the Yukon and Amazon Rivers (percent)

Physical form of chromium	Amazon River	Yukon River
In solution and organic complexes	10.4	12.6
Adsorbed	3.5	2.3
Precipitated and coprecipitated	2.9	7.2
In organic solids	7.6	13.2
In crystalline sediments	75.6	64.5

Source: Adapted from Gibbs, 1973, Table 1, p. 72. Reprinted by permission of the publisher.

The trace-element mass balance for the Walker Branch Watershed, Oak Ridge, Tennessee, showed that the six-month atmospheric input of chromium for soil and water was 22.1 g/ha and the total stream output was 9.1 g/ha, giving a retention in the watershed of 58.8% (Andren, Lindberg, and Bate, 1975). The suspended load in water also provides a major transport mechanism for chromium in this watershed (67.6% of chromium is in insoluble form).

Movement of metals can occur through aquifers. Pinder (1973) demonstrated that simulation of movement of groundwater contaminants can be obtained with the Galerkin-finite element method. This method was used for chromium-contaminated groundwaters of Long Island, New York.

As with chromium in air and soil, the exact chemical form of chromium in water is not well defined. In contrast to soil, the small concentration of organic matter in some streams is insufficient to reduce chromium(VI) to chromium(III), and thus both chromium(III) and chromium(VI) ions exist. Ultimately, however, chromium(VI) is reduced to chromium(III), which precipitates and is eventually deposited in sediments.

Mobilization of chromium can occur following the discharge of suspended matter carried by rivers into estuaries (De Groot and Allersma, 1973). This process, which has been demonstrated for the Rhine Estuary, apparently occurs because the organic matter onto which chromium had been adsorbed decomposes and the metals are released as soluble organo-metallic complexes. As De Groot pointed out, this release may be the result of specific conditions in the Rhine Estuary and may not generally occur in all estuaries. Some data support the contention that salinity does not greatly affect the distribution of chromium between soluble and suspended phases. In a study by Evans and Cutshall (1973), about 94% of ^{51}Cr was in dissolved form in river water; after addition of seawater to river water, about 92% still remained in the dissolved form. Seawater did not leach ^{51}Cr from suspended river matter (<1%) even after three weeks of contact time. Similarly, seawater did not leach ^{51}Cr from bottom sediments of the Columbia River (Johnson, Cutshall, and Osterberg, 1967).

Schroeder and Lee (1975) studied transformations between chromium(III) and chromium(VI) in natural waters. They found that only 3% of chromium(III) was oxidized by O_2 in 30 days at ambient temperatures (22°C to 26°C). The presence of manganese oxide increased rates dramatically but the significance of this fact in natural waters is doubtful due to calcium and magnesium saturation of reaction sites. Many compounds reduced chromium(VI). The authors recommended that total chromium, not chromium(III), be used to assess water quality because of possible transformations. The arguments are not very convincing.

In the Upper James Bay Estuary, chromium is apparently removed from water by adsorption to hydrous iron oxides and clay materials (Van Horn, 1973). The form of chromium in the water was not reported. Lu and Chen (1976) found that chromium was not significantly released from sediments into seawater under either oxidizing or reducing conditions.

Krauskopf (1956) addressed the problem of factors controlling the low concentrations of rare metals in seawater. Seawater is "undersaturated" in rare metals in spite of the large amounts supplied. Removal of chromium(VI) by adsorption to $Fe_2O_3 \cdot nH_2O$, apatite, clay, and plankton varied from about 10% to 47%, while $MnO_2 \cdot nH_2O$ was very effective, adsorbing between 89% and 94% of the initial chromium(VI). Chromium(VI) is the major stable form of chromium in seawater (Cutshall, Johnson, and Osterberg, 1966; Fukai, 1967).

Adsorption and precipitation as sulfides could not account for the low concentrations observed; however, Krauskopf (1956) suggested that in sulfide-rich or reducing areas, chromium(VI) is converted to chromium(III) and is then precipitated as $Cr(OH)_3$. This approach is oversimplified because chromium input is not entirely in the form of chromium(VI), nor is it all in soluble form; thus, some chromium settles into sediments.

The identification of chromium sources and the quantification of input into waters has not been well studied. Bruland et al. (1974) concluded that it was "not possible to evaluate the contribution from different transporting agencies — winds, sewer outfalls, storm runoff, and river runoff" for basins of the southern California coast. Fluxes of chromium into sediments of the San Pedro, Santa Monica, Santa Barbara, and Soledad basins had a yearly average of 2.9 $\mu g/m^2$ for anthropogenic chromium input and 5.2 $\mu g/m^2$ for natural chromium input. Annual washout flux of chromium from atmosphere to water was calculated to be about 0.1 $\mu g/m^2$. Thus, while Winchester and Nifong (1971) concluded that the major input of chromium into Lake Michigan was particulate deposition from airborne sources, the major input of chromium into the California basin was from entering waters.

Chelating agents, such as nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA), release metal cations from sediments. Clay Lake (Ontario) sediments, extracted by 10% NTA and EDTA solutions at a ratio of 1 to 10, contained 190 and 210 ppb chromium, respectively, while distilled water extract contained only 8 ppb chromium (Barica, Stainton, and Hamilton, 1973). At NTA concentrations of 1 mg/liter, little difference was observed in extractable chromium compared to distilled water controls; however, some other metals were released in the order of Fe > Mn > Zn > Pb > Cu > Cr. Since NTA may be used as a phosphate substitute in producing detergents, the environmental impact of the release of NTA into waters is of concern.

Concentrations are projected to be as high as 200 ppb NTA in some natural waters. Natural and metallo-chelated forms of NTA are ultimately broken down to nitrates, which may also become a problem. Actual rates of degradation depend upon the particular NTA-metal complex (Chau and Shiomi, 1972). Degradation time of a chromium-NTA complex in Lake Ontario water, pH 8.2, was six days.

7.5 WASTE MANAGEMENT

Chromium wastes released to air, land, and water are produced by several major industries (Figure 7.1). By far the largest amount is released into water during treatments involved with the plating and finishing industries (Table 7.9). In most cases, these waters must be treated before being discharged. Since the maximum permissible chromium concentration in public water supplies has been set at 0.05 ppm by the U.S. Environmental Protection Agency, efficient chromium removal from wastewaters, especially water from plating industries, and disposal of the chromium obtained are necessary.

Chromium concentrations in various water wastes were 10,000 to 50,000 ppm in bright dip wastes from metal plants, 600 ppm in pickle bath or plating wastes, 40 ppm in leather industry wastes, and 10 to 60 ppm in cooling-tower blowdown waters (Cheremisinoff and Habib, 1972). The major technique for chromium removal from these waters is by precipitation. Chromium(VI) is usually first reduced to chromium(III) with ferrous sulfate, sodium bisulfite or metabisulfite, or sulfur dioxide at low pH values (Ottinger et al., 1973). The pH is then raised to about 9.5, and chromic hydroxide and other metal hydroxides precipitate. The precipitate is collected in settling ponds, dried, and then disposed of by landfill, ocean dumping, or incineration. At present, recovery of chromium from these precipitates is not economically feasible. Ion exchange, another process which can remove chromium from wastewaters, is not used as extensively as precipitation, but it may be feasible in certain cases, especially where the flow rate can be adequately controlled.

Some chromium wastes are discharged into municipal sewers and can help precipitate sulfide from water. Such chromium wastes are usually reduced to chromium(III) and precipitated during transit to the sewage plant. This precipitate is removed by sewage treatment processes. Other removal methods, such as precipitation, ion flotation, electro-chemical conversion, electrodialysis, activated carbon adsorption, liquid-liquid extraction, and reverse osmosis are being developed and may be commercially used in the future.

Combinations of two or more methods may be necessary for more effective concentration reductions. Furthermore, novel advances in technology may produce versatile methodology. For example, Netzer, Wilkinson, and Beszedits (1974) reported that discarded pulverized automobile tires effectively removed chromium from solutions, and when preceded with a lime precipitation step, reduced chromium concentrations to below 0.1 ppm (99% removal) over the pH range 6 to 11.

Each disposal method for precipitated wastes as well as municipal wastes poses potential problems involving release of chromium to the environment. Leaching is the primary means by which chromium is removed from landfill and could possibly contaminate groundwater and surface waters. Leachate from simulated sanitary landfills, however, did not contain measurable amounts of chromium (Pohland, 1975). Care must be taken to avoid acidification of the landfill, which would solubilize a portion of the trivalent chromium and thus allow it to be leached out.

Incineration is another method for disposal of municipal wastes. Municipal incinerators in Milwaukee, Wisconsin, produced stack effluents which contained 0.1% to 1.0% chromium in ash (Jens and Rehm, 1966). Collector catch and residues each contained 0.01% to 0.1% chromium. Over a five-day period, 5.3 metric tons of dry stack emissions was produced from the incineration of 1281 metric tons of refuse (variable water content). Impinger-water residues (obtained from a sampling train for measuring particulates in stack emission of incinerators) contained <0.5 ppm chromium (Achinger and Daniels, 1970). The magnetic metallic fraction of the residue from municipal solid waste incinerators contained an average of 0.009% chromium (0.001% to 0.0187% range) (Ostrowski, 1971). A portion of the chromium may have come from discarded tin-free steel beer cans, which have been reported to contain 60 ppm chromium (0.12 lb/ton).

Wastewater from plating industries does not contain just chromium, however, and an integrated procedure for efficient removal of all metals in the wastewater must be developed. A flow diagram for precipitation treatment of wastes (Figure 7.5) illustrates the steps necessary to produce a low-contamination effluent from a plating company (Cave, 1971). Watson (1973) gave a more detailed examination of all methods of hexavalent chromium removal from water and the current level of technology for each method.

The overall efficiency of chromium removal from sewage influent varied from 17% to 78% (average 37%) in a study of seven midwestern sewage treatment plants (Brown et al., 1973). Systems with primary treatments averaged only 27% removal, a trickling-filter secondary treatment effected 38% chromium removal, and an activated sludge secondary treatment removed 78% of the chromium. From sewage influent (no influent chromium data listed), the Hyperion Wastewater Treatment Plant in Los Angeles produced primary effluent containing about 300 ppb chromium and a secondary effluent containing 60 ppb chromium (activated sludge process and sedimentation) (Chen et al., 1974). Approximately 60% of chromium in the primary effluent and 30% in the secondary effluent were in particulate form. Concentrations of dissolved chromium (defined as that passing through a 0.2-μm filter) in two samples dropped from 147 and 100 ppb in primary effluent to 30 and 47 ppb in the secondary effluent, reductions of 80% and 53%, respectively. Particle size distribution for primary effluent was 19% of total chromium retained on 0.2- to 8-μm filters, 75% on 8- to 44-μm filters, and 6% on >44-μm filters. For the secondary effluent, 33% was retained on 0.2- to 8-μm filters, 51% on 8- to 44-μm filters, and 16% on >44-μm filters. Discharge from the plant consisted of primary effluent, mixtures of primary effluent and secondary effluent, and mixtures of effluent and digested sludge. The composite sample of final effluent released contained about 200 ppb chromium; about 50% of the chromium in the final effluent was retained on filters with pore size of less than 8 μm.

In New York City, about 676 kg/day (0.04 to 0.50 ppm influent chromium concentration) is discharged into wastewaters and received at various sewage plants (Klein et al., 1974). Most of the chromium was discharged from the metal-plating industry, although contributions also came from other sources (for example, residential wastewaters, 0.008 to 0.15 ppm chromium; surface runoff, 0.16 ppm chromium). Of the total chromium received at sewage plants, 43% came from electroplaters, 9% from other industries, 9% from runoff, 28% from residential sources, and 11% was unaccounted for. Sewage plant discharge effluent contained from 0.04 to 0.19 ppm chromium (weighted average 0.08 ppm), representing a 48% reduction in chromium content of the water. Estimates of chromium in waters discharged to the harbor were 353 kg/day for sewage plant effluents, 313 kg/day for runoff, and 259 kg/day for untreated wastewater, totaling 925 kg/day of discharge (about 0.12 ppm chromium, weighted average). Harbor waters contained from <0.5 to 10 ppb chromium, while the adjacent regions contained about 0.5 ppb; area rivers contained from <0.5 to 5.8 ppb.

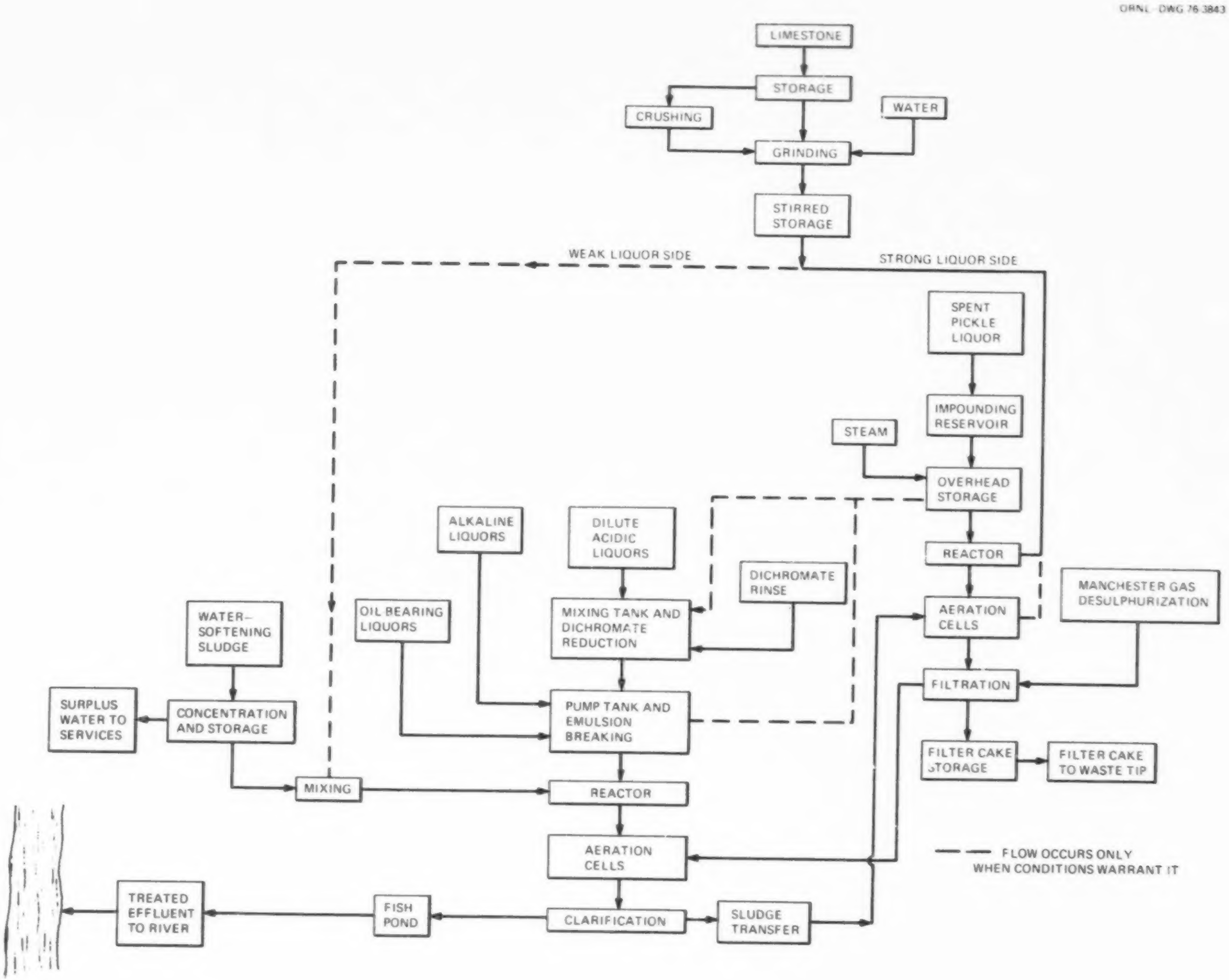
ORNL-DWG 76-3843
LIMESTONE
STORAGE
CRUSHING
WATER
GRINDING
STIRRED STORAGE
WEAK LIQUOR SIDE
STRONG LIQUOR SIDE
SPENT PICKLE LIQUOR
IMPOUNDING RESERVOIR
STEAM
OVERHEAD STORAGE
REACTOR
AERATION CELLS
MANCHESTER GAS DESULPHURIZATION
FILTRATION
FILTER CAKE STORAGE
FILTER CAKE TO WASTE TIP
ALKALINE LIQUORS
DILUTE ACIDIC LIQUORS
DICHROMATE RINSE
OIL BEARING LIQUORS
MIXING TANK AND DICHROMATE REDUCTION
PUMP TANK AND EMULSION BREAKING
WATER-SOFTENING SLUDGE
SURPLUS WATER TO SERVICES
CONCENTRATION AND STORAGE
MIXING
REACTOR
AERATION CELLS
TREATED EFFLUENT TO RIVER
FISH POND
CLARIFICATION
SLUDGE TRANSFER
FLOW OCCURS ONLY WHEN CONDITIONS WARRANT IT

Figure 7.5. Flow diagram for precipitation treatment of wastes. Source: Adapted from Cave, 1971, Table 2, p. 207. Reprinted by permission of the publisher.

In some waste treatment facilities, stabilization ponds are used to remove various elements from effluent (Bulthuis, Craig, and McNabb, 1973). Organisms in the ponds help to produce a purified water supply. Data from a study of such ponds in Michigan showed that chromium concentration of the effluent dropped from 8.5 to 3.5 ppb as water moved from an anaerobic pond, to a facultative pond, to a facultative-aerobic pond, and then to an aerobic pond. Of the total chromium entering into the facultative-aerobic and the aerobic ponds, between 1% and 2% was incorporated into higher plant materials and 18% to 20% was incorporated into sediments. Thus, some chromium was immobilized during the purification process.

Sewage sludge contains a wide range of chromium concentrations (Table 7.25) — from about 20 ppm to over 40,000 ppm, with a mean concentration range of 86 to 380 ppm (Page, 1974). In a study of 42 sludges from England, chromium (but not other metals) was found to increase in concentration with the size of the city; apparently, the amounts chiefly reflected the use of chromium compounds in the tanning industry (Berrow and Webber, 1972). Most of the chromium in sludge, however, is in insoluble form. In a study of the effluents from sludge, Argo and Culp (1972) reported that while sand filtration only reduced the concentration of chromium(VI) from 50 to 49 ppb, carbon adsorption reduced the concentration to 17 ppb. Lime coagulation, which was only slightly more effective than the sand filtration, only reduced the chromium(VI) from 56 to 50 ppb in one effluent. Total chromium concentrations of sewage effluents in 57 Michigan treatment plants studied by Page (1974) were in the range of 0.0005 to 1.46 ppm (median 0.02 ppm), most of which was soluble (0.01 to 1.0 ppm, median 0.02 ppm). Available chromium (defined as being soluble in 2.5% acetic acid) in 42 sewage sludges from England ranged from <0.9 to 170 ppm (mean 22 ppm, median 4.4 ppm) (Berrow and Webber, 1972). This amount was between 0.7% and 8.5% of the total chromium content of sludge and was considerably higher than the 0.01 to 1.0 ppm in 2.5% acetic acid extracts of soils.

As mentioned earlier, most of the chromium in sludge is insoluble and apparently remains so during treatment. Blakeslee (cited in Page, 1974) studied the concentrations of trace elements, including chromium, in sludges from a number of sewage treatment plants at various stages of treatment. Undigested sludge contained from 66 to 7800 ppm chromium, secondary digestor sludge from 22 to 9600 ppm, and vacuum filter cake from 28 to 10,600 ppm. Although mass balances were not given, these figures, when considered with the generally low chromium concentrations in sewage effluents, infer that chromium in sludge is solubilized to only a small extent by the treatment the sludge undergoes.

The application of sewage sludges to soils presents both advantages (source of irrigation water, plant nutrients, improvements of properties, reclamation of wastewater) and disadvantages (e.g., potential toxicity of trace elements); however, few references present data concerned with chromium in sludge-amended soils. Seven years after sludge application was discontinued (66 metric tons of sludge per hectare per year for 19 years; the 0.5 *N* acetic acid—extractable concentration of sludge was 3.5 ppm chromium), the 0.5 *N* acetic acid—extractable content of soil was 2.6 ppm chromium compared to the 0.9 ppm chromium from untreated soil (Le Riche,

Table 7.25. Chromium concentrations in sewage sludge

Locale	Number of sludges	Chromium concentration (ppm dry wt)			Number of samples in concentration range			
		Range	Mean	Median	1-10 ppm	10-100 ppm	100-1,000 ppm	1,000-10,000 ppm
Sweden	93	20-40,615	872	86	0	48	39	2
Michigan	57	22-30,000	2,031	380	0	19	18	18
England	42	40-8,800	980	250	0	13	19	10
Southern California		<40-600						
Toronto, Canada		60-16,000						
Oklahoma		0-600						
Indiana		50-19,600						

Source: Modified from Page, 1974, compiled from Tables 1, 2, 3, and 5, pp. 9, 11, 12, and 15.

1968). No information was found on the chemical form of chromium in sludge, sewage effluents, or sludge-amended soils.

Trace elements supplied by sludge added to soils are slowly removed by processes such as leaching, plant uptake, and runoff. For example, at two different sludge application rates, total amounts of 118 and 164 ppm chromium were added to soils over a three-year period, yet at the end of this period only 26% and 19%, respectively, of chromium added was recovered (Page, 1974). Le Riche (1968) found that extractable chromium (0.5 *N* acetic acid) in sludge-amended soils decreased little over an eight-year period after the last sludge application (2.8 ppm for 1959 and 2.6 ppm for 1967). Chromium concentrations of water "saturation" extracts of sludge (0.01 ppm), of soil beneath sludge drying ponds (0.01 to 0.40 ppm), and of soil from fields irrigated with sewage effluent (0.01 to 0.40 ppm) were within the range found for extracts of a wide variety of soils. Nevertheless, these data indicate that a certain amount of chromium can be removed from amended soils and transported in drainage water (Page, 1974).

SECTION 7

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SECTION 8

ENVIRONMENTAL INTERACTIONS AND THEIR CONSEQUENCES

8.1 SUMMARY

Chromium is released to the environment from many sources and is cycled among air, land, and water; small amounts are taken up by a wide variety of organisms. Although environmental interactions of chromium have been inadequately studied, chromium does not appear to be biomagnified in either aquatic or terrestrial food chains, even though certain organisms can accumulate it. The relative immobility of chromium in biological systems, due to the poor solubility of a number of its compounds, partially explains the lack of biomagnification observed.

The average daily chromium intake for humans is approximately 100 μg. Most of this amount is the result of dietary intake; lesser amounts are contributed by water and air. This chromium, however, may not be in a form available for utilization by man. Few studies exist on the chromium content of organisms growing in polluted regions, but the general trend seems to be an increased chromium content in lower trophic level organisms in response to an increased environmental level of chromium.

8.2 ENVIRONMENTAL CYCLING

Data on removal rates from each medium are given in Section 7. Chromium released into the atmosphere, either as chromate mist from cooling towers or plating operations or as particulate matter from ore extraction processes or incineration of chromium-bearing materials, is eventually deposited on land or water. In soil which has low pH and contains organic matter, hexavalent chromium is reduced to trivalent chromium; in well-aerated water with little organic matter, hexavalent chromium is more stable and can persist.

Soil chromium is generally in an insoluble, unavailable form, mainly either as the weathered form of parent chromite or as $Cr_2O_3 \cdot nH_2O$. A small amount of soil chromium is water extractable and slightly larger amounts are extractable with ammonium acetate or acetic acid. Therefore, leaching could be expected to remove only a small amount of soil chromium; however, literature on the quantitative aspects of this process is sparse. Surface runoff into waters can be expected to remove a small amount of soil chromium.

Surface runoff, deposition from air, and release of wastewaters (variously treated for chromium removal) are sources of chromium in waters. Sedimentation is apparently an effective removal mechanism, as shown by the very low concentrations of chromium in most waters. Chromium, therefore, accumulates in sediments. In rivers, considerable suspended material which contains chromium can be transported and eventually deposited in estuaries or bays.

8.3 HUMAN EXPOSURE

Human exposure to chromium in the general environment occurs mainly through the diet. The amount of chromium ingested per day depends on the amount of food ingested and the chromium content of each food. Estimates of the amount of chromium ingested have come from analyses of institutional diets. One such study for institutions in the United States showed the average chromium content of all foods served to be between 0.175 and 0.472 mg/kg (Murthy, Rhea, and Peeler, 1971). Statistical analysis of the data showed significant variation in chromium amounts from one sampling period to the next and from one institution to another. Average amounts ingested daily ranged from 0.455 to 0.880 mg chromium. During 1967, the average amount of chromium consumed was about 0.63 mg/day; the amount consumed was slightly less in summer than in fall and spring.

An average of 0.019 mg chromium per lunch (range of 0.009 to 0.088 mg per lunch) was found in school lunches sampled from 300 schools in 19 states (Murphy, Page, and Watt, 1971). Schroeder, Balassa, and Tipton (1962) found 0.078 mg chromium in a one-day institutional diet. Thus, studies estimating daily dietary intake of chromium are in agreement.

The chromium content of a variety of foods is presented in Table 8.1 (Thomas, Roughan, and Watters, 1974), Table 8.2 (Schroeder, Balassa, and Tipton, 1962), Table 8.3 (Meranger and Somers, 1968; Meranger, 1970; Zook et al., 1976), and Table 8.4 (Toepfer et al., 1973). The chromium data presented by these five research groups show fair agreement for most foods. The results of Thomas, Roughan, and Watters (1974) showed a range from <0.01 to 1.13 ppm chromium with a mean of 0.15 ppm for fresh foods and 0.23 ppm for frozen vegetables. Schroeder, Balassa, and Tipton (1962) gave a range of 0.01 to 0.13 ppm chromium for fruits and vegetables with a mean of 0.03 ppm, and Toepfer et al. (1973) found chromium amounts between 0.04 and 0.27 ppm in vegetable samples. Thomas, Roughan, and Watters (1974) expressed concern about the chromium concentrations in these reports; while they found a nickel content similar to that reported by Schroeder, Balassa, and Tipton (1962), they found higher chromium and lower cobalt values. Murphy, Page, and Watt (1971) observed wide geographical and seasonal variation in trace element content of total diets, which could explain the discrepancies. The nutritional significance of chromium in diets is discussed in Section 6.3.2.

Community air and drinking water contribute smaller quantities of chromium to the total daily exposure than does the diet. In the Community Water Supply Survey (CWSS), only 4 of 969 water supplies exceeded the U.S. Public Health mandatory limit of 50 ppb chromium (Section 7.3.4). Since the CWSS did not present concentration data for the finished drinking water supplies, it is difficult to determine amounts of chromium actually received from drinking water. A reasonable estimate from the discussion in Section 7.3.4 is about 10 ppb. If a daily intake of 1 to 2 liters of water is assumed (Friberg et al., 1974), consumption of chromium from drinking water would be between 10 and 20 μg/day.

The need for caution in interpretation due to analytical uncertainty in these results must be kept in mind. Large errors are found in current

Table 8.1. Chromium content of fruits and vegetables

Food	Number of samples	Chromium content (ppm)	
		Range	Mean
Fresh fruits and vegetables			
Beetroot	2	0.04-0.12	0.08
Broccoli	5	0.06-0.33	0.19
Brussels sprouts	19	0.01-0.64	0.14
Cabbage	23	0.05-0.29	0.15
Carrots	10	<0.01-0.13	0.08
Celery	3	0.08-0.12	0.11
Cucumber	3	0.15-0.20	0.17
Leeks	3	0.02-0.16	0.08
Lettuce	2	0.12-0.21	0.17
Mushrooms	6	0.06-0.72	0.25
Onions	11	0.04-0.83	0.19
Potatoes	14	0.06-0.40	0.15
Spinach	2	0.12-0.28	0.20
Swedes	8	<0.01-0.19	0.09
Watercress	7	0.05-0.31	0.16
Miscellaneous	8	<0.01-0.15	0.08
Dried herbs	6	<0.01-0.22	0.11
Apples			
Skin	2	0.07-0.13	0.10
Flesh	4	0.06-0.16	0.11
Pears			
Skin	7	0.20-0.50	0.30
Flesh	7	0.07-0.32	0.18
Whole fruit	6	0.23-0.88	0.44
Plums	6	<0.01-0.01	<0.01
Rhubarb	5	0.01-0.09	0.04
Tomatoes	10	0.16-0.37	0.24
Total	179	<0.01-0.88	0.15
Frozen vegetables			
Peas	6	0.12-1.13	0.38
Spinach	2	0.03-0.09	0.06
Beans	5	0.17-0.24	0.22
Sweet corn	2	0.35-0.39	0.37
Broad beans	3	0.11-0.40	0.22
Brussels sprouts	3	0.08-0.25	0.16
Asparagus	3	<0.01	<0.01
Total	22	<0.01-1.13	0.23

Table 8.1 (continued)

Food	Number of samples	Chromium content (ppm)	
		Range	Mean
Canned fruits and vegetables			
Apples	7	<0.01-2.64	1.39
Apricots	3	0.02-0.08	0.04
Black currants	4	0.02-0.08	0.03
Grapefruit	3	0.01-0.07	0.04
Oranges	3	<0.01-0.05	0.02
Peaches	4	0.03-0.06	0.05
Prunes	6	0.53-2.15	1.01
Damsons	2	0.72-2.04	1.39
Plums	12	<0.01-2.64	1.04
Pineapples	5	0.02-0.09	0.04
Rhubarb	8	0.01-1.84	0.66
Tomatoes	4	0.02-0.04	0.03
Baked beans	7	<0.01-0.64	0.24
Sweet corn	3	0.06-0.54	0.22
Spinach	7	0.01-0.08	0.04
Asparagus	3	<0.01-0.18	0.11
Mushrooms	3	0.23-0.47	0.33
Total	84	<0.01-2.64	0.39

Source: Adapted from Thomas, Roughan, and Watters, 1974, Table 1, p. 774, Table 2, p. 774, and Table 3, p. 775. Reprinted by permission of the publisher.

chromium analyses (Section 2), and it is likely that older data are even less reliable. Until the reasons for the analytical problems are discovered, we will not know how much reliance to place on these numbers.

The quantity of chromium inhaled varies with the environment. No measurable chromium was found in rural air, whereas urban air contained values up to 0.1 μg/m³ (Section 7.3.2). A more reasonable estimate for chromium concentrations in urban air would be about 0.01 μg/m³ (Section 7.3.2). If one assumes that an individual inhales about 20 m³ of air per day (Friberg et al., 1974), then airborne chromium exposure would be about 0.2 μg/day for each individual.

Therefore, total daily chromium intake approximates 100 μg per individual; food accounts for about 80 μg of this amount. This level of exposure apparently does not cause any chromium toxicity symptoms. Indeed, daily supplements of 250 μg chromium have been used to improve glucose tolerance in cases of malnutrition (Section 6.3.1.1).

Table 8.2. Chromium content in various foods

Food sample	Chromium content (ppm)
Condiments and spices	
Pepper, black	3.70
Thyme	10.00
Cloves	1.50
Chili powder	0.86
Green pepper, whole fresh	0.19
Red pepper, whole, fresh, hot	0.01
Salt, table	0.0
Salt, sea	0.0
Dairy products	
Milk, whole, homogenized	0.01
Milk, dried, skim	0.07
Eggs, hen	0.16
Butter	0.17
Cheese, Wisconsin swiss	0.11
Mean	0.10
Meat and fish	
Haddock	0.02
Halibut, meat	0.01
Halibut, skin	0.18
Lobster, claw meat	0.0
Lobster, tail meat	0.0
Lobster, digestive gland	0.33
Lobster, shell	0.0
Oyster, canned, gulf	0.09
Clams, hard shell	0.44
Clams, soft shell	0.36
Shrimp, fresh	0.01
Scallop, fresh	0.11
Beef marrow	0.03
Beef chuck	0.09
Lamb chop	0.12
Pork chop	0.10
Partridge gizzard	0.13
Chicken gizzard	0.11
Chicken breast	0.26
Chicken skin	0.27
Tripe	0.04
Mean, excluding skins, shells, and organs	0.11

Table 8.2 (continued)

Food sample	Chromium content (ppm)
Vegetables	
Potato, white	0.0
Beans, dried, navy	0.08
Beans, dried, yellow-eye	0.05
Beans, wax	0.03
Beans, green string	0.02
Lentils, dried	0.09
Beets	0.01-0.03
Radishes	0.0
Parsnips	0.13
Parsnip leaves	0.08-0.19
Turnip leaves	0.04-0.06
Carrots	0.0-0.03
Onions	0.01-0.02
Spinach	0.0-0.05
Swiss chard	0.06
Squash, summer	0.02
Cucumber	0.01-0.03
Kohlrabi	0.0
Cauliflower	0.02
Cabbage	0.01-0.06
Sauerkraut	0.03
Rhubarb, raw	0.02
Rhubarb, cooked in stainless steel	0.05
Lettuce, garden	0.07
Lettuce, head	0.02-0.13
Mean	0.03-0.05
Fruit	
Peach, Elberta, raw	0.01
Peach, stewed in stainless steel	0.01
Raisins	0.02
Blackberries, wild	0.0
Tomato, raw	0.01
Tomato, stewed in stainless steel	0.14
Apple, MacIntosh	0.02
Pear	0.01
Plum	0.02
Cranberry jelly	0.0
Mean	0.02

Table 8.2 (continued)

Food sample	Chromium content (ppm)
Grains and cereals	
Corn, fresh on cob	0.02
Corn meal	0.05
Corn flakes	0.04
Corn oil margarine	0.37
Corn oil	0.47
Vegetable shortening	0.16
Rye, seed	0.05
Rye, whole	0.04
Flour, wheat (all purpose)	0.0
Wheat, whole	0.03
Flour, wheat (Japanese)	0.0
Wheat, whole (Japanese)	0.08
Rice (Japanese) 204 samples	0.04
Rice	0.05
Oatmeal, dry	0.06
Mean, excluding fats	0.04
Animal food	
Dog food pellets	4.24
Rat diet, special	0.07-0.17

Source: Adapted from Schroeder, Balassa, and Tipton, 1962, Table 6, pp. 949-950. Reprinted by permission of the publisher.

8.4 BIOMAGNIFICATION IN FOOD CHAINS

Examination of the chromium content in organisms of higher trophic levels in known food chains has not shown significant biomagnification. Chromium is a relatively immobile element in biological systems, as exemplified by the lack of gastrointestinal absorption of chromium(III) compounds (Section 6.2.1.2) and by lack of translocation of chromium from the site of absorption in plants (Section 4.2.3). This immobility may partially explain the lack of biomagnification observed. Lack of biomagnification could also occur because the chromium content of foods for a particular trophic level is highly variable.

8.4.1 Terrestrial Food Chains

Little information was found on the chromium concentration in components of terrestrial food chains. In a study of forest food chains, concentration data of selected components showed no large biomagnification. However, according to Andren et al. (1973), such data "must be viewed cautiously, since specific dietary constituents and food chain linkages were

Table 8.3. Chromium content of selected seafoods and fruit juices

Food sample	Chromium content (ppm)	Reference
Salmon	0.47	Meranger and Somers, 1968
Clam chowder	0.71-0.85	Meranger and Somers, 1968
Tuna	0.13	Meranger and Somers, 1968
Oyster	0.58	Meranger and Somers, 1968
Sardine	0.35-0.37	Meranger and Somers, 1968
Crab meat	0.57	Meranger and Somers, 1968
Channel catfish, wild	0.12	Zook et al., 1976
Pacific halibut	0.18	Zook et al., 1976
Ocean perch	0.10	Zook et al., 1976
Spiny lobster	0.14	Zook et al., 1976
Alaskan shrimp	0.15	Zook et al., 1976
Atlantic scallops	0.05	Zook et al., 1976
Grape juice	0.08	Meranger, 1970
Prune juice	0.15	Meranger, 1970
Hawaiian Punch, pineapple, apple, orange, grapefruit juices	<0.01	Meranger, 1970
Tangerine juice	<0.01	Meranger, 1970
Lime juice	0.24	Meranger, 1970
Lemon juice	0.05	Meranger, 1970

not determined." Table 8.5 gives the chromium concentration in selected components of a typical forest ecosystem. Earthworms and cryptozoa contained high chromium concentrations, but more data are necessary to determine if specific organisms feeding on earthworms or cryptozoa biomagnify chromium.

8.4.2 Aquatic Food Chains

Aquatic ecosystems are easier to study than terrestrial ecosystems and more information exists for them. In an experimental study of "an unnatural and simple, but reproducible, food chain" under controlled environmental conditions, Baptist and Lewis (1969) found that concentration levels of ^{51}Cr-labeled trivalent chromium declined through the food chain. The chain

Table 8.4. Chromium content of selected food samples and biological value of extracts containing chromium

Sample	Total solids (%)	Chromium content			Biological activity[a]			
		Total		Chromium removed with 50% ethanol (%)	Acid hydrolysate		50% Ethanol extract	
		Wet wt (ppm)	Dry wt (ppm)		Biological value	Chromium (ppm)	Biological value	Chromium (ppm)
Meats and fish								
Liver, calf's	30.2	0.55	1.77	33.6	2.95	0.220	1.88	0.077
Beef, round	34.1	0.57	1.67	18.7	2.60	0.220	1.65	0.044
Chicken, breast	29.2	0.11	0.37	24.6	2.42	0.086	3.19	0.054
Chicken, leg	26.2	0.18	0.70	21.9	1.99	0.146	2.41	0.080
Shrimp	15.2	0.07	0.48	69.4	0.91	0.059	3.46	0.101
Haddock	19.8	0.07	0.34	51.5	1.24	0.053	2.26	0.052
Lobster tail	19.9	0.05	0.23	93.6	2.06	0.007	5.09	0.065
Oysters	12.2	0.26	2.16	30.2	1.95	0.089	1.56	0.013
Grains, grain products								
Wheat, grain	88.7	0.28	0.32	37.8	2.29	0.022	2.08	0.042
Wheat, germ	94.6	0.23	0.24	85.0	1.82	0.024	1.55	0.020
Wheat, bran and middlings	91.1	0.38	0.42	15.8	2.08	0.030	1.58	0.003
Wheat, flour	90.2	0.23	0.25	14.3	1.86	0.018	1.40	0.002
Bread, white	62.2	0.26	0.42	42.9	2.98	0.077	1.47	0.008
Bread, whole wheat	64.5	0.42	0.66	32.8	2.26	0.023	1.25	0.005
Bread, rye	62.7	0.30	0.49	29.7	1.70	0.027	2.15	0.039
Spaghetti	91.4	0.15	0.16	75.0	2.34	0.006	1.38	0.012
Cornflakes	94.3	0.14	0.15	80.0	1.60	0.014	1.09	0.011
Cornmeal, yellow	91.2	0.10	0.11	74.8	3.18	0.021	2.02	0.040
Cornmeal, white	91.1	0.12	0.13	47.0	1.80	0.024	1.44	0.028
Grits	90.0	0.05	0.06	90.6	2.19	0.011	2.43	0.027
Fruits								
Bananas	27.3	0.10	0.38	99.5	2.02	0.056	0.99	0.057
Apple, peel	18.6	0.27	1.48	52.5	2.65	0.258	1.04	0.064
Apple, pared	14.4	0.01	0.09	40.0				
Oranges	14.7	0.05	0.31		2.30	0.064		
Strawberries	8.5	0.03	0.34	80.7	1.95	0.029		
Blueberries	22.0	0.05	0.22		2.96	0.060		
Vegetables								
Carrots	11.6	0.09	0.78	26.5	1.92	0.101		
Green beans, snap	8.2	0.04	0.48	100	2.33	0.192		
Potatoes, old	47.4	0.27	0.55	48.0	1.75	0.076		
Potatoes, new	37.0	0.21	0.57	53.6	1.72	0.077		
Spinach	9.4	0.10	1.03		1.91	0.200		
Miscellaneous								
Mushrooms	3.7	0.04	1.27	86.6	1.88	0.169	3.19	0.147
Yeast, brewer's	95.8	1.12	1.17	48.2	3.34	0.070	4.06	0.007
Cheese, American	61.9	0.56	0.92	30.4	1.39	0.034	1.40	0.024
Beer	4.6	0.03	0.61	100	3.60	0.083	1.66	0.063
Vegetarian								
Choplets	20.1	0.10	0.48	24.6	1.18	0.077	3.72	0.047
Chicken slices	21.5	0.07	0.32	87.8	1.15	0.055	2.86	0.090
Pepper								
Black, table	90.5	0.35	0.38	100	2.35	0.076	1.99	0.076
Chili, fresh	23.4	0.30	1.28	22.5	2.81	0.120	1.82	0.068
Butter	85.4	0.13	0.15	80.0	1.32	0.030	1.20	0.010
Margarine	90.9	0.18	0.20	50.0	1.35	0.070	1.28	0.008
Milk, skimmed	9.5	0.01	0.13	84.4	1.00	0.030	1.90	0.032
Ginger ale	10.5	<0.01	0.05		2.74	0.023		
Sugar, cane	100		0.02					
Egg white	12.2	0.08	0.65	36.0	1.20	0.088	1.08	0.048
Egg yolk	47.8	1.83	3.84	50.4	1.59	0.065	0.96	0.025

[a] See Section 6.4.2 for discussion of biological activity.

Source: Adapted from Toepfer et al., 1973, Table 1, p. 71. Reprinted by permission of the publisher.

consisted of the alga *Chlamydomonas* sp. (first trophic level), brine shrimp *Artemia salina* (second trophic level), post-larval croaker (*Micropogon undulatus*) or post-larval mojarra (*Eucinostomus* sp.) (third trophic level), and the mummichog (*Fundulus heteroclitus*) (fourth trophic level). Measurable uptake of ^{51}Cr from water was observed for all trophic levels; however, for *Artemia* and the mummichog, uptake through food was much greater, whereas post-larval fish accumulated slightly more ^{51}Cr from water than from food.

Mathis and Cummings (1973) also found decreased chromium concentrations in higher trophic level organisms of aquatic ecosystems (about 10 ppm in worms, about 5 ppm in clams, about 1.2 ppm in omnivorous fish, and about 1 ppm in carnivorous fish).

Table 8.5. Chromium concentration in selected trophic levels of a forest ecosystem in East Tennessee

Ecosystem component	Chromium concentration (ppm dry wt)
Substrate	
Soil	7
Litter	2
Producers	
Tree leaf	4
Tree branch	0.3
Tree root	9
Acorn	0.1
Consumers	
Insect	3
Squirrel	0.8
Sparrow	1
Mouse	1
Predators	
Hawk	1
Owl	0.2
Omnivores	
Crow	1
Oppossum	0.6
Fox	0.8
Cryptozoa	10
Earthworm	5

Source: Adapted from Andren et al., 1973.

In the Tamar River, Tasmania, chromium concentrations in the Pacific oyster *Crassostrea gigas* (average 7.9 ppm chromium, dry wt basis) were poorly correlated with concentrations of chromium in the mud (average 87.8 ppm chromium, dry wt basis) (Ayling, 1974). According to Ayling, "accumulation factors describing the ability of oysters to concentrate heavy metals, based upon their ability to extract metals dissolved in water, appear meaningless, where there are high concentrations of metals in muds." Since the contribution to total chromium intake of chromium dissolved in water, of chromium in particulates filtered from water, and of chromium in ingested muds is unknown, an accumulation factor is difficult to determine. The author pointed out that microorganisms within the muds may have concentrated heavy metals by adsorption and thus made them more available to the oyster. No data were found to either support or refute this contention.

Concentration of heavy metals in fecal material in water may allow for biomagnification in certain food chains. Boothe and Knauer (1972) studied the concentration of a number of metals, including chromium, in the feces of the crab *Pugettia producta*, which feeds on the brown alga *Macrocystis pyrifera*. While the concentration ratios (concentration in feces to concentration in the alga) were >2 for cobalt, arsenic, zinc, copper, lead, and iron, the ratio for chromium was 0.8, which indicated no concentration of that element in the fecal pellet.

Davis, cited in Foster (1963), showed that lower trophic levels in the Columbia River ecosystem (algae, sponges, insect larvae, and snails) have higher concentrations of ^{51}Cr than do higher trophic levels (fish and crayfish). Levels of ^{51}Cr in the organisms of various trophic levels were observed to be higher in winter than in summer (Watson et al., 1971). The ^{51}Cr is released into the river from the cooling waters used in the Hanford reactors. Sodium dichromate is added to the reactor water as a corrosion inhibitor and becomes radioactive due to neutron bombardment. This ^{51}Cr can also enter terrestrial ecosystems through sorption by crops grown on lands irrigated with Columbia River water (Perkins et al., 1960). Concentrations of about 1 μμCi/g of ^{51}Cr were found in several crops; however, milk and meat of cattle did not contain measurable amounts. No ^{51}Cr activity could be detected in humans who lived in the area and consumed these foods.

Lack of assimilation of chromium present in foods is probably the major reason organisms of the higher trophic levels contain lesser amounts of chromium. In fact, the poor absorption of chromium by many animals makes ^{51}Cr-labeled trivalent chromium a valuable tracer when used in conjunction with ^{14}C for measuring assimilation efficiencies (Calow and Fletcher, 1972).

SECTION 8

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SECTION 9

ENVIRONMENTAL ASSESSMENT

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9.1 SUMMARY

In attempting to arrive at a satisfactory estimate of the ecological distribution of chromium and its present fate and effect on man's environment, a number of factors must be carefully considered. Paramount among these is the past and present state of the art in relation to the analytical methods employed for the analysis of chromium. In order to scientifically and objectively determine environmental pathways, concentration factors and biomagnification, and human health related factors, the basic data base must be as accurate as possible. Unfortunately, the analytical methods used in the past years for all of the studies involving chromium, especially in many environmental media and plant and animal tissue, leave much doubt as to the accuracy and validity of the data base. Even today the results from many laboratories are questionable. This point cannot be over stressed, since inaccurate and even erroneous conclusions can be drawn using such data, especially older literature data. For example, only recently has chromium been accepted as an essential element for man and its role in the maintenance of the glucose tolerance factor established. An interesting comment is that nutritionists have greater concern for marginal deficiency of chromium in humans than to overexposure. The basic reason behind the relative lateness of this discovery was the lack of a sensitive analytical method for the measurement of chromium at low levels. However, the data base is rapidly improving with the development and adoption of new analytical procedures in more laboratories. Enough data do exist to be able to determine, on a semiquantitative basis, that chromium as far as the total environment and the general population are concerned, does not represent an environmental hazard. However, in the occupational setting, exposure to chromium, especially in its hexavalent form, does represent a potential health hazard and worker exposure should be limited.

The National Institute of Occupational Safety and Health recommends two standards for hexavalent chromium designed to protect the health and safety of workers up to a 10-hr workday, 40-hr workweek, over a working lifetime. One standard addresses occupational exposure to a group of noncarcinogenic, but otherwise hazardous, materials. The other pertains to those instances where there is exposure to chromium(VI) materials associated with an increased incidence of lung cancer.

The problem is that there is no practical way, on the basis of chemical analysis of airborne chromium(VI), to distinguish between noncarcinogenic and carcinogenic chromium materials. Thus for all practical purposes, all airborne chromium(VI) shall be considered to be carcinogenic. The current NIOSH recommended standard for carcinogenic chromium(VI) is 1 μg chromium(VI)/m^3 of air. On the basis of current information, this recommended standard appears to be reasonable and obtainable in the workplace and is thought to be adequate to protect the health of workers.

In summary, at present and with the available data, chromium does not, except in the occupational setting, appear to be present in the general environment in significant enough concentrations to cause concern. Pathways have yet to be determined for the ecological cycling and fate of chromium and considerable research in these areas needs to be done. The major area of needed research is the development of sensitive analytical techniques capable of distinguishing between the various valence states and species of chromium. This is a critical need due to the vast differences in the potential toxicity of chromium, especially the differences between chromium(III) and chromium(VI).

9.2 QUANTITY OF CHROMIUM ENTERING VARIOUS ENVIRONMENTAL MEDIA

No chromium ore is currently mined in the United States. Chromite imports were estimated at 1,800,000 metric tons in 1972. United States chromium consumption for the same year was 320,000 metric tons (Morning, 1974) of chromium, which corresponds to about 1,000,000 metric tons of ore. The difference between the import and consumption figures represents re-export of chromium in the form of manufactured products, increases in stockpile storage, and uncertainties in the consumption estimates. For example, Brantley (1970) estimated 1968 consumption at 458,000 metric tons of chromium, the GCA corporation (1973) gave the 1970 demand as 389,000 metric tons, and the above estimate of 320,000 was for 1972. The figures show almost a 50% reduction in consumption over a four-year-period which is obviously not an accurate assessment of the trend. Chromium consumption is increasing and is expected to continue to increase at least until the year 2000.

Industrial uses of chromium are about 64% in metallurgy, 20% in the manufacture of refractories, and 16% in the chemistry industry. The primary chromium chemicals are sodium chromate and sodium dichromate. These are converted as needed for many uses, including chrome plating, as an oxidant in many synthetic processes, in leather tanning, as a component of many pigments, in fungicides and wood preservatives, and as rust and corrosion inhibitors.

Chromium emissions into the atmosphere are estimated to be between 11,000 and 16,000 tons/year in the United States. Ferrochromium production is the major source (about 68%) with ore refining, chemical processing, and refractory processing all making major contributions. Sources of atmospheric chromium not directly related to industrial uses of the metal include coal and oil combustion, cement production incineration, and asbestos production. Coal combustion is by far the largest contributor from these "inadvertent" sources and was estimated to contribute 1420 metric tons in 1970. Coals contain a wide range of chromium concentration: Illinois coals contain from 4 to 54 ppm with an average of 14 ppm; a Belgian study reported 12 to 55 ppm in coals; and the Allen Steam Plant, burning coal containing 21 ppm chromium, produced slag containing 180 ppm and precipitated fly ash with 356 ppm. Chromium used for corrosion inhibition contributed to the atmospheric contamination around cooling towers, but the total amount is not very large and the effect quite local.

Geographic distribution of atmospheric chromium closely parallels areas of high population and industrial activity. Four of the EPA regions, the Great Lakes and three East Coast regions, received over 80% of the total emissions. Nonindustrial regions received very little.

The primary source of soil contamination is fallout and washout from the atmosphere. Some soil chromium is added with fertilizers reported to contain 175 ppm to 344 ppm. Sewage sludge can contribute significant amounts of chromium when used as a fertilizer. Natural levels of chromium in soils is reasonably high and quite variable, with 64% in the range 25 ppm to 85 ppm total chromium. Serpentine soils may contain several percent chromium. Except for local situations, anthropogenic activity does not appear to have altered soil chromium levels. Most soil chromium, whether natural or added, is quite insoluble and not readily available to plants.

The plating and finishing industries are a major source of chromium in industrial waters. They accounted for 43% of the chromium input in New York sewage. Residential runoff accounted for 21% of the influent, possibly due to atmospheric chromium that had settled. The overall loss of chromium from the plating process is about 20,000 metric tons/year and only about 30% is recycled. Discharges from the tanning and textile industries also contribute chromium to waters.

The total amount of chromium transported by rivers is surprisingly large; for example, 790 metric tons/year by the Susquehanna River. However, most of it is in the rather insoluble trivalent form and closely associated with sediments. When sediments are deposited, the chromium is not readily mobilized. It remains effectively adsorbed and/or precipitated and is unavailable to biological systems.

9.3 JUDGMENT OF POTENTIAL TOXICITY

The toxicity of chromium is almost exclusively a problem of industrial activity and in most cases the effects are relatively local. The metal is quite toxic to fish and many other aquatic organisms, especially in its hexavalent form which can persist in waters low in organic matter. Aquatic organisms vary widely in their sensitivity to the element. The lethal level for some invertebrates is 0.05 ppm while tests on other organisms, including fish, indicate that several tens of ppm can be tolerated. Maximum permissible concentrations must be set, of course, based on the more sensitive organisms.

In the presence of organic matter, hexavalent chromium is reduced to the less toxic and relatively insoluble trivalent form in natural waters. The trivalent chromium precipitates with, or is adsorbed on, sediments where it is much less active biologically.

Evidence of toxicity to plants in practical environmental situations includes reduced growth of tobacco exposed to cooling tower drift (Section 4.3.2). A 75% reduction of leaf area occurred at 15m and 200m from the tower. Some evidence indicates that high chromium levels contribute to the low fertility of serpentine soils, but other factors such as low calcium content and low calcium to magnesium ratio are probably more serious. Wastes from chromium smelting can be highly toxic to plants (Section 4.3.1). In one example, as little as 1% of the waste in sand completely inhibited germination. The affected area had to be covered with 25 cm to 30 cm of soil for successful revegetation.

9.4 TOXICITY AND HUMAN HEALTH EFFECTS

The available information on the toxic effects of chromium compounds on humans comes almost entirely from known occupational exposures to hexavalent chromium. Reports in the literature date back as far as 1827.

Chromium as a metal is essentially biologically inert and has not produced any known toxic or other harmful effects in either man or laboratory animals. Trivalent compounds of chromium have no established toxicity. They are poorly absorbed when ingested orally and do not give rise to local or systemic effects; exposure by inhalation has not demonstrated any measurable biological effect. The trivalent compounds do react with the skin by combining with proteins in the superficial layers, but they do not cause ulceration. There are no known effects of trivalent chromium on animals or humans exposed to normal levels of chromium generally found in uncontaminated environmental media. The primary reason for the nontoxic nature of the trivalent compounds of chromium is their extreme insolubility. As discussed in Section 6.3, feeding of trivalent chromium to experimental animals at levels of even hundreds of milligrams daily failed to produce toxic symptoms. In fact, other studies have found only beneficial effects of feeding small amounts of trivalent chromium in lifetime studies with rats and mice. It can be generally concluded, therefore, that chromium in its trivalent form does not represent a potentially harmful chemical in man's environment.

Hexavalent chromium compounds, on the other hand, do represent potentially hazardous chemicals in the environment and exposure must be controlled, especially in the occupational environment. These compounds when ingested, inhaled, or absorbed are toxic even to the point of being carcinogenic. The toxic nature of hexavalent chromium is discussed in detail in Section 6 of this report.

There are presently three standards recommended by NIOSH for the control of worker exposure to various forms of chromium. These standards have been recommended after careful review of existing data and represent the best opinion on safe levels of airborne chromium. They are considered adequate to protect the health and safety of workers.

The first of these recommended standards pertains to chromic acid, defined as chromium trioxide [chromium(VI) oxide or chromic acid anhydride] and aqueous solutions. The NIOSH criteria document for chromic acid contains the following recommendations: Occupational exposure to chromic acid shall be controlled so that no worker is exposed either to (1) a concentration of chromic acid greater than 0.05 mg as chromium trioxide/m^3 of air determined as a time-weighted average exposure for an 8-hr workday, 40-hr workweek, or (2) a ceiling concentration in excess of 0.1 mg as chromium trioxide/m^3 of air as determined by a sampling time of 15 min.

The other two NIOSH recommended standards pertain to hexavalent chromium, defined as the chromium in all materials in the +6 (hexavalent) state. One standard addresses occupational exposure to a group of noncarcinogenic, but otherwise hazardous materials, while the other pertains to occupations and workplaces where there is exposure to other chromium(VI) materials associated with an increased incidence of lung cancer.

On the basis of the chemical analysis of airborne chromium(VI) materials, there is no practical means of distinguishing between these two groups of chromium(VI) materials. Until the airborne chromium(VI) in a particular workplace is demonstrated by the employer to be of the type considered noncarcinogenic, all airborne chromium(VI) shall be considered to comprise carcinogenic materials.

According to the NIOSH criteria document for chromium(VI), noncarcinogenic chromium(VI) is the chromium(VI) in monochromates and bichromates of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium(VI) oxide. Carcinogenic chromium(VI) comprises any and all chromium(VI) materials not included in the above noncarcinogenic group.

The recommended standard is as follows:

(1) Carcinogenic chromium(VI) shall be controlled in the workplace so that the airborne workplace concentration of chromium(VI), sampled and analyzed according to recommended procedures, is not greater than 1 μg chromium(VI)/m^3 of breathing zone air.

(2) Noncarcinogenic chromium(VI) shall be controlled in the workplace so that the airborne workplace concentration is not greater than 25 μg chromium(VI)/m^3 of breathing zone air determined as a time-weighted average (TWA) exposure for up to a 10-hr workday, 40-hr workweek, and is not greater than 50 μg chromium(VI)/m^3 of breathing zone air as determined by any 15-min sample.

The present levels of hexavalent chromium found in the general environment do not appear to pose a human health problem; however, continuous monitoring and further epidemiological research is needed, especially in relation to levels of hexavalent chromium in public water supplies.

Present environmental levels of chromium in urban ambient air (0.01 to 0.03 μg/m^3; in soils (traces to 250 ppm); in seawater (below 0.1 ppb); in river water (1 to 10 ppb); in municipal drinking water (nondetectable — 35 ppb); and in foods (0.02 to 0.22 μg/g) are not of sufficiently high concentration to cause concern. The total chromium intake per day in man, estimated as between 5 to 115 μg in food and water and 0.04 to 0.08 μg in air, has not demonstrated any measurable toxic effect even at the subclinical level. If chromium is a problem it is probably because many U.S. diets are regarded as at least marginally deficient in chromium.

It is evident from the available data that chromium does not, currently, appear to represent a significant hazard in the general environment. Occupational exposures do represent potential and real problems and need to be controlled.

However, as recommended by the National Academy of Sciences report on chromium, because some chromium compounds have caused serious health problems in persons through industrial exposure and because the hexavalent compounds are irritating and corrosive to tissue, the role of chromium in the environment requires careful consideration and much future research needs to be developed.

9.5 PERSISTENCE IN THE ENVIRONMENT

Chromium is an element and is therefore not going to decompose into harmless substances as many organic pollutants do. In that sense, it might be regarded as infinitely persistant. In most natural systems, chromium(III) is the most stable form of the element. In the presence of organic matter, chromium(VI) is reduced, probably aided by complexation of the resultant chromium(III). Chromium(III) is characterized by limited solubility near neutral pH due to formation of hydrated oxides, and by a strong tendency to sorb onto clays, sediments, and organic matter.

Atmospheric chromium falls out or is washed out into soils or water. In aqueous systems the trivalent form of the element either precipitates or is adsorbed onto particulate matter or organic matter. In either case, it is rather quickly removed and is found in sediments. The hexavalent form is stable only in waters with little organic matter. In all other cases, it is reduced and later precipitated. In soil, hexavalent chromium is reduced to trivalent form and is then tightly bound to clay particles. It is not readily leached except at low pH. Uptake by most plants is poor and there is very little translocation to the above ground parts.

Few experiments on specific environmental sinks have been reported, probably because the sinks, primarily soil and sediments, are fairly predictable from known chemistry of the element. In some cases the element may bind to organic matter temporarily, but the binding is transferred to soil or sediment particles as the organic matter decomposes. There is little evidence that chromium(III) is likely to be oxidized to the more soluble and toxic hexavalent state under environmental conditions.

9.6 CRITICAL ENVIRONMENTAL PATHWAYS

Conditions under which harmful levels of chromium are likely to persist in the environment include the following:

a. Chromium(VI) is stable in water which is low in organic matter. The chromates remain in solution and are quite toxic to certain aquatic organisms, especially invertebrates.

b. An accepted method for removing chromium from wastestreams is reduction followed by precipitation of chromium(III) hydroxide. The precipitate is often disposed of in land fills. There appears to be little leaching from the fills under normal conditions, but acid leach water could be expected to solubilize and transport the chromium.

c. Chromates are used as corrosion inhibitors in cooling-tower water and are subsequently deposited on the surrounding area as the mists drift from the tower. The surrounding land and any vegetation growing on it are contaminated by the airborne hexavalent chromium. Elevated chromium levels in plants have been reported up to 1200m from a tower. It is not known how much was deposited directly on the plants and how much was due to uptake from the soil. Chromium deposited on plants apparently remains in the hexavalent form and most of it can be washed off by rain. In the soil the chromium(VI) is reduced and bound as discussed earlier. No reports detailing harmful effects due to cooling tower drift were found.

d. Sewage sludge is often put on soil and some sludges are quite high in chromium. The element remains tightly bound to the sludge and/or soil and is neither readily leached nor taken up by plants. However, some reports indicate increased chromium levels in plants grown on sludge amended soil. Again, no reports of harmful effects to the vegetation or to animals that consumed it were found.

e. Large amounts of chromium are transported by major rivers, nearly all of which are associated with particulates, and most probably results from natural weathering.

f. Large amounts of chromium are released to the atmosphere from the ferro-chromium and other industries as well as from fossil fuel combustion. There is no evidence that these releases constitute a health hazard.

9.7 BIOMAGNIFICATION

No evidence exists for the biomagnification of chromium in food chains. Animals in the higher trophic levels tend to have lower tissue chromium concentrations than their prey. If the hexavalent state is ingested by man or animals it is probably reduced in the stomach. Trivalent inorganic chromium is inefficiently absorbed in the digestive tract of animals, while chromium in certain organically bound forms is readily absorbed by the mammalian digestive system. The most significant of these forms is the glucose tolerance factor. Organically bound chromium is also readily transferred across the placenta to the fetus in contrast to very poor transfer of the inorganic form. These facts are of profound significance in nutritional aspects of the essential trace element chromium, but probably have little bearing on chromium as an environmental contaminant.

9.8 SUMMARY OPINION AND RESEARCH NEEDS

At the present time, using data available from industrial and epidemiological studies, chromium does not appear to represent an environmental hazard to the general population. Occupational exposures require that levels be controlled to the point that the health and safety of the worker is not affected. Trivalent chromium in either case does not appear to represent a potential hazard.

Future research is required with a view to not only potential overexposure, but also regarding deficiency. Almost no data exist concerning the ecologic cycling of chromium in the environment. Data on the chemical valence of chromium in the ecosystem and the environment are not available. Analytical techniques do not exist for species identification and accurate determination of the chemical form of chromium in complex media, especially in biological tissue. These questions can only be answered by properly designed and executed research.

SECTION 9

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16. ABSTRACT

This report is a review of the scientific literature on the biological and environmental effects of chromium. Included in the review are a general summary and a comprehensive discussion of the following topics as related to chromium and specific chromium compounds: physical and chemical properties; occurrence; synthesis and use; analytical methodology; biological aspects in microorganisms, plants, wild and domestic animals, and humans; distribution mobility and persistence in the environment; assessment of present and potential health and environmental hazards; and review of standards and governmental regulations. More than 500 references are cited.

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